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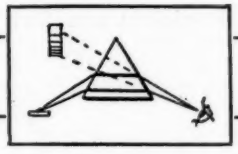

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On the Optical Anisotropy of Molecular Crystals. I. Experimental*

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(Received June 15, 1933)

IF an anisotropic vector property of a molecule is unmodified by the presence of other molecules in a condensed system a pragmatic theory can be formulated correlating the structure of the medium with the properties of its constituent parts. This fortunate condition is realized in the diamagnetic anisotropy of crystalline solids,[1] but fails to obtain for the optical properties. It is possible, however, that certain "apparent" optical susceptibilities of a compound can be found which will take molecular interaction into account and thus permit extension of the theory. Such "apparent" values can be obtained from liquids and applied to solids provided the surroundings of a molecule are effectively similar in the two phases. This assumption can be tested by comparing the mean optical susceptibilities of a solid with that of its melt. It is our purpose to present measurements on a number of compounds that will permit this comparison to be made.

It was necessary for us to develop experimental methods for determining densities and refractive indices of molecular compounds. Incidental to the main object the dispersions of the refractive indices were measured over a limited range. Aromatic compounds, with but one exception, were selected for study since their molecular anisotropies are inherently great. Preference was given to hydrocarbons on account of the possibly small molecular interaction for such substances. The majority of the compounds studied were ones for which the refractive indices and densities of the melts had previously been determined.

PREPARATION OF CRYSTALS

Large single crystals were required for determinations of refractive indices and small flawless pieces were needed for density evaluations. Both these criteria can readily be met by crystals grown from melts, provided that the compound used does not decompose under such conditions. Crystals grown from solution are often small and plastic, while voids are almost always present.

We have prepared crystals from melts after the method of I. Obreimow and L. Schubnikow[2] which is a modification of methods devised by G. Tammann. The various compounds were melted and sealed in thin-walled glass tubes, about 1.5 cm in diameter, the ends of which were drawn down to sharp points. These tubes, in turn, were placed in a small vertical furnace, the tempera-

* A paper dealing with the theoretical aspects of this problem will be published elsewhere.

[1] K. S. Krisknan, B. C. Guha and S. Banerjee, Phil. Trans. Roy. Soc. **A700** (1933).

[2] I. Obreimow and L. Schubnikow, Zeits. f. Physik **25**, 31 (1924). See also I. Obreimow and A. Prichotjko, Phys. Zeits. d. Sow. **1**, 203 (1932).

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ture of which was maintained from 10°–40° above the melting point of the compound used. Cooling, with initial crystallization in the sharp point, was effected by slowly lowering the tube and its contents from the furnace. Single crystals a centimeter or greater on an edge were usually obtained. The method of S. Kyropolous[3] was used for preparing some crystals of naphthalene but low thermal gradients made the process somewhat difficult.

Crystals of hexamethylene tetramine and hexamethyl benzene were grown from solution since they decompose upon melting. Some crystals of dibenzyl were grown by cooling saturated solutions of the compound in alcohol. The crystals prepared were shown to be stable forms by comparing their optical properties with those of stable crystals obtained from solutions.

Most of the compounds used were pure substances, in contradistinction to technical, purchased from the Eastman Chemical Company. Crystals of benzoic acid and naphthalene were grown from standard calorimetric samples prepared at the U. S. Bureau of Standards. The melting points of the various compounds were within 2° of those reported in the literature. Further purification, from all impurities save ones present in solid solution, was effected in the preparation of the crystals. An impurity has only a differential effect on the density of a crystal. The refractive indices of a substance with a very high birefringence, however, might be sensitive to minor impurities since the orientations of the molecules might be altered. This possibility was tested, and found to be absent, on naphthalene crystals grown from melts to which small amounts of benzoic acid had been added.

Densities

The chief systematic errors that have limited the accuracy of most density determinations on crystalline compounds are the presence of voids and of foreign inclusions in the samples used, the purity of the materials, and the surface occlusion of air. The suspension method developed by Retgers[4] reduces errors arising from imperfections of the crystals to a minimum. The purity of the material and the occlusion of air are under the control of the experimentor.

Convection currents in the suspension medium limit the accuracy of Retgers' method as ordinarily applied to a probable error of about 0.001 in density. If the gravitational potential is increased, however, the limit can readily be lowered by an order of magnitude, to 0.0001. In order to accomplish this we have used a centrifuge giving a centrifugal force of about 4×10^2 times the force of gravity at a radius of 10 cm, which was the mean radius for a tube 8 cm long. Hydrostatic pressure alters somewhat the densities of the medium and sample in motion and thus necessitates a minor correction which can be as great as 0.0001. The correction is a differential one in that the compressibilities of the crystals and the suspending mediums might be somewhat different. Most of the compounds that we have examined are ones for which this differential correction is of the order of 1×10^{-5} and is thus quite negligible.

The density observations in general were made on a large number of apparently flawless crystal fragments about one mm on the edge. These were further graded, as suggested by Retgers, by suspending in a medium in which imperfect crystals floated. The densities were then determined on the selected materials by suspension in various salt solutions, such as KI in water. Seven to ten independent observations were made at temperatures constant to within $\pm0.6°$. In order to avoid psychologically persistent errors the densities for alternate determinations were approached from opposite sides in solutions of densities considerably different, say 0.05, from that of the substance. Close temperature regulation was not needed, which is probably contrary to the opinion of the casual reader, since the variations in densities were of the order of 0.0001 and accidental. A treatment of our results according to Bayes theorem[5] leads to probable errors that are less than 0.0001. This procedure is justifiable in that the same accidental errors affect each set of observations.

The accuracy of this method is to be compared with that usually claimed for values obtained by

[3] S. Kyropolous, Zeits. f. anorg. Chemie **54**, 308 (1926).
[4] J. W. Retgers, Zeits. f. physik. Chemie **3**, 289 (1889).
[5] *Note:* W. E. Deming, Phil. Mag. (In press).

the method of Andrea.[6] The centrifugal suspension method, however, is perhaps susceptible to further refinement. It might be desirable, for instance, to have a very shallow centrifugal cell and to make all observations on a moving system by means of a stroboscope.

In order to test for possible systematic errors in the method it was considered advisable to carry out a number of control experiments. The only substance for which the density is known with considerable accuracy is calcite of analyzed purity. J. A. Bearden[7] has given 2.71030 ± 0.00003 g cm^{-3} at 20°C as its density. The indicated probable error was arrived at by assuming that the density variations in different samples are experimental. This is not borne out by inspection of "probable errors" for specific samples; thus samples, showing a probable error in the density of *ca.* 0.00004 in each case, have an overall variation of 0.0002. The materials, although very pure, contained about 0.02 percent (FeO+MnO), which might have caused an error of 0.00005 in the observed densities. The most consistent value for four out of six samples given by Bearden is 2.7102.

The results of seven observations that we have made on the density of calcite from Iceland using C_6H_5Br and $C_2H_2Br_4$ mixtures as the suspending mediums are:

	$t°$		$t°$
2.71012	24.6	2.70985	24.3
2.70945	24.6	2.70998	24.6
2.70909	24.5	2.71043	24.3
2.71096	25.5		

The mean value is 2.70998 at 24.6°. The maximum deviation is 0.00098 and the estimated r.m.s. error is 0.00023. This value corrected to 20° by the formula $\rho = \rho_0(1+0.0000139\ t)$ is 2.7101. Since the compressibility of calcite is negligible compared to that of the suspending medium it is necessary to add a correction of 0.0001 to this value, giving 2.7102 as the final value.

Calcite was really an unsuitable reference substance since its density is much greater than those of the various compounds studied and thus requires a somewhat different technique. For this reason a number of intercomparisons were made with the compounds themselves without an absolute base of reference. In the case of diphenyl a different sample was taken for each of seven observations. The corresponding values for the density are listed in Table I together with values for naphthalene determined on only two samples.

TABLE I.

Diphenyl	$t°$	Naphthalene	$t°$
1.17560	24.2	1.17841	24.3
1.17466	24.9	1.17928	23.4
1.17544	24.4	1.17908	24.4
1.17520	24.1	1.17896	23.7
1.17455	24.4	1.17886	23.7
1.17470	24.8	1.17955	23.4
1.17507	24.8	1.17900	24.2
		1.17875	24.4
		1.17860	24.5
		1.17896	23.2
Mean 1.1750	24.5°	Mean 1.1789	23.9°

The densities of a large single crystal of naphthalene weighing about 0.91 g and a less perfect crystal of diphenyl weighing about 6.64 g were determined by displacement of water. The mean values of seven determinations for these obviously imperfect crystals were 1.1775 at 24.1°, and 1.1725 at 24.1°, respectively. The density of naphthalene was also determined, by displacement of water, on two polycrystalline samples that had been compressed as pellets at 10,000 kg cm^2. The initial values were 1.1742 and 1.1782, decreasing over a period of three months (probably on account of the formation of minute cracks) to 1.1612 and 1.1627, respectively. It is perhaps apparent that such methods give results that are lower, by some parts in a thousand, than the values obtained by suspension on selected material.

Dibenzyl grown from the melt was compared with crystals obtained from solution. The observed values are given in Table II. The values

TABLE II.

Melt	$t°$	Solution	$t°$
1.10213	22.8	1.10162	23.4
1.10230	23.4	1.10162	23.2
1.10190	23.9	1.10190	23.8
1.10180	24.0	1.10186	23.5
1.10205	23.8	1.10167	23.4
Mean 1.1020	23.6°	Mean 1.1017	23.5°

[6] *Note:* E. Cohen and W. A. T. Cohen, K. Akad. van Weten de Amsterdam **35**, 1255 (1932).

[7] J. A. Bearden, Phys. Rev. **38**, 2089 (1931). See also O. K. Defoe and A. H. Compton, Phys. Rev. **25**, 618 (1925).

TABLE III. *Summary of optical data.*

Substance, formula and molecular weight	t°C	Index	Indices of refraction for various wave-lengths							Density		Mean refractive index of the solid at the density of the liquid for λ=5876 or 5890	Mol refractivity for λ=5876 or 5890	2V Calculated axial angle
			4861A	5016	5461	5780	5876	6563	6676	t°C			After Lorenz-Lorentz	
Benzoic acid C_6H_5COOH 122.067	23.1	γ		1.7113		1.6989	1.6975			23.3	1.3211		35.6134	64° 24′ (5876)
	23.1	β		1.6246	1.6174	1.6144	1.6120						32.1197	
	23.1	α		1.5941	1.5880	1.5830	1.5815	1.5745	1.5741				30.8149	
Dibenzyl C_6H_5-CH_2-CH_2-C_6H_5 182.151	131.9	Liquid[16]	1.51777				1.5080*	1.49867		131.9	1.0738	1.4906	33.8865	
	24.4	γ			1.7638	1.7593	1.7566			23.4	1.1019		67.7924	88° 42′ (5876)
	23.0	β			1.6330	1.6296	1.6286		1.6215				58.7107	
	23.5	α		1.5382	1.5329	1.5300	1.5292		1.5252				50.9989	
Hexaethylbenzene $C_6(C_2H_5)_6$ 246.287	80.6	Liquid[16]	1.55257				1.5379*	1.53385		80.6	0.9416	1.5275	60.4984	
	23.5	γ		1.6259		1.6144	1.6135			24.2	0.9942		86.2832	71° 00′ (5876)
	23.5	β		1.5358	1.5312	1.5289	1.5285						76.3399	
	23.5	α		1.4971		1.4898	1.4901		1.4853				71.6338	
Hexamethylene tetramine $C_6H_{12}N_4$ 140.144	130.4	Liquid[16]	1.48686				1.4772*	1.47357		130.4	0.8305	1.4407	83.8225	
	23.7		1.5984	1.5953	1.5917	1.5899	1.5893		1.5856	24.3	1.3390		35.2870	
Pentamethylbenzene $C_6H(CH_3)_5$ 148.157	23.5	γ			1.6304	1.6266			1.6188	23.5	1.0046		51.7236	81° 50′ (5780)
	23.5	β			1.5892	1.5858			1.5789				49.0045	
	23.5	α			1.5602	1.5571			1.5508				47.0393	
Diphenyl $(C_6H_5)_2$ 154.114	107.2	Liquid[16]	1.49932				1.4889*	1.48484		107.2	0.8472	1.4810	50.4636	
	24.0	β			1.6598	1.6555	1.6542			24.5	1.1750		48.0845	
	24.0	α	1.5737	1.5702	1.5641	1.5610	1.5598	1.5550	1.5547				42.3986	
Naphthalene $C_{10}H_8$ 128.092	77.1	Liquid[16]	1.60760				1.5884*	1.58112		77.1	0.9896		52.4391	
	24.3	β			1.7255	1.7196	1.7182		1.7077	23.9	1.1789		42.8322	
	24.3	α		1.5333	1.5291	1.5249	1.5238		1.5188				33.2339	
p-Dibromobenzene $C_6H_4Br_2$ 235.881	99.6	Liquid[17]	1.60378				1.5828*	1.57509		99.6	0.9641		44.3908	
	24.0	β		1.7594	1.7498	1.7455	1.7437		1.7375	24.2	2.2836		41.8151	
	24.0	α			1.5716	1.5690	1.5682		1.5642				33.8021	
Hexamethylbenzene $C_6(CH_3)_6$ 162.176 Resorcinol $C_6H_4(OH)_2$ 110.065 Catechol $C_6H_4(OH)_2$ 110.065	99.3	Liquid[17]	1.58939				1.5744*	1.56897		99.3	1.8201		42.7893	
	23.5	γ		1.7344	1.7255	1.7211	1.7199		1.7114	24.8	1.0630		60.2515	50° 24′ (5780)
	23.5	β		1.6918	1.6847	1.6802	1.6791		1.6713				57.5950	
	23.5	α			1.4835	1.4816			1.4773					
		γ^{18}					1.6273†				1.285		30.3707	45° 20′ (5890)
		β^{18}					1.6197†						30.0756	
		α^{18}					1.5781†						28.4289	
	133.6	Liquid[16]	1.56219				1.5475*	1.54261		133.6	1.1642	1.5394	30.0042	
		γ^{18}					1.7336†				1.375		32.0702	33° 14′ (5890)
		β^{18}					1.6139†						27.8955	
		α^{18}					1.6044†						27.5468	
	132.0	Liquid[16]	1.54411				1.5301*	1.52524		132.0	1.1372	1.5160	29.9018	

Substances for which densities only were determined:

Substance	*t°C*	*Density*
Acenaphthene	24.8	1.2195
p-Toluidine	24.8	1.1249
o-Toluic Acid	24.0	1.2996
Benzene	−8.6	1.0235

* Interpolated value.
† Measured by Heydrich for λ=5890A.

obtained from the melted material are slightly the greater of the two. Crystals grown from alcohol were sufficiently perfect to use as prisms for determining refractive indices and were apparently flawless.

An attempt was made to test the suspension method by comparing the experimentally determined density with that calculated from the dimensions of the unit cube of hexamethylene tetramine. This quantity was calculated from the angles of reflection of Cu $K\alpha_1\alpha_2$ radiation for the 1st and 2nd orders from (110). If the absolute wave-length of Cu $K\alpha_1\alpha_2$, mean, is taken as 1.5440A[8] the value of ρ is 1.333 if Avogadro's number is taken as 6.064×10^{23} [9] and the atomic weights of C, H, N, and O as 12.003, 1.00777, 14.0083, and 16.0000, respectively. If Cu $K\alpha_1\alpha_2$ has an absolute wave-length of 1.5417A[10] the value of ρ is 1.339. These values are in substantial agreement with the experimental value, 1.3390, which was obtained from a large number of apparently flawless crystals deposited in a solution of hexamethylene tetramine.[11]

The results that we have obtained are summarized with the optical properties in Table III. The values listed are hardly to be compared with results previously reported in the literature, of which no exhaustive survey is intended. P. Groth[12] gives the various densities as: naphthalene 1.152–1.153; diphenyl 1.189; benzoic acid 1.322; *p*-dibromobenzene 2.220–2.280. The density of naphthalene given by J. Dewar[13] as determined from displacement of air is 1.1589 (17°). K. Yardley[14] gives 1.042 (18.5°) as the density of hexamethyl benzene. Krishnan, Guha and Banerjee[1] determined densities by the ordinary Retgers' method and found: Naphthalene, 1.081; diphenyl, 1.132; dibenzyl, 1.086; and acenaphthalene, 1.191.

Indices of Refraction

The most satisfactory methods for determining the refractive indices of a biaxial substance are minimum deviation with a prism and total reflection from a flat surface. A serious difficulty in applying these methods to molecular compounds is that a high vapor pressure effectively prevents the preparation of a surface, by the ordinary methods, that is suitable for measurements. This is almost unsurmountable if, as is usually the case, prisms are required other than those formed by developed faces. We have developed a simple technique for overcoming this difficulty in the preparation of surfaces for use in the total reflection method.

A flat surface with a rather high polish can be prepared by melting. An approximately flat surface is ground on a large single crystal from a melt. This is placed on an optically flat surface which is then gently heated until the crystal surface melts, wetting the mount. It is then cooled and as it cools the thin melted layer resolidifies apparently as a part of the single crystal. The crystal, when it has cooled to room temperature, can be lifted from the surface. It is immediately placed on the refractometer, speed being essential, and used for measurements. After some experience about half of the prepared surfaces were suitable for use.[15]

We have used an Abbe-Pulfrich crystal refractometer manufactured by R. Fuess and Company, Berlin-Steglitz. The index of refraction of the hemisphere is 1.9149 for Na_D and the dispersion of the glass is accurately known. The least count of the scale is 1′ and it is supplied with a tangent screw, graduated in 6″, to be used as a slow motion and for the measurement of dispersion. The mounting liquid used was

[8] M. Siegbahn, *Spektroskopie der Röntgenstrahlen*, 2nd edition, Berlin, 1931, p. 62 after measurements of E. Bäcklin.

[9] R. T. Birge, Rev. Mod. Phys. **1**, 1 (1929).

[10] J. A. Bearden, Phys. Rev. **37**, 1210 (1931).

[11] *Note:* It perhaps is of some value to point out that observations on hexamethylene tetramine might serve to give an excellent value of *e* since the lattice characteristics which affect such measurements in the case of calcite are probably not operative, the atomic weights of the constituent elements are accurately known, the volume of the unit of structure depends on a single constant, a long wave-length can be used, very pure crystals of requisite size can be obtained and the line width might not be too great.

[12] P. Groth, *Chemische Krystallographie*, Leipzig, 1919, Vols. 4 and 5.

[13] J. Dewar, Chem. News **91**, 216 (1905).

[14] K. Yardley, Proc. Roy. Soc. **A123**, 494 (1929).

[15] *Note:* We have prepared some flat surfaces by the usual grinding and polishing methods. Polishing can be accomplished by the use of the thinnest possible soft kid leather mounted on a flat glass plate; the usual ring method being employed for preventing undue rounding at the edges.

Rohrbach's solution, in glycerine-water mixtures, with n *ca.* 1.77. A liquid was available for use up to the limit of the hemisphere but the organic substances were readily soluble in it and moreover, on solution, precipitated a film on the hemisphere. Measurements were made on both sides of the scale and for both positions of the crystal for the particular limiting curve. The majority of the measurements were made with a mercury vapor lamp and a helium discharge tube, Corning filters being available for giving sufficiently monochromatic light.

In order to guard against serious errors, as have been made by some other workers, independent approximate measurements of the refractive indices were made by the immersion method under the microscope. Since the birefringences of the majority of the compounds examined are extremely high it was thought best to prevent, as far as possible, preferred directions of growth, crystal distortion, cleavage, etc. This was accomplished by grinding a fused mass at liquid air temperatures and then carefully mounting the powder for observation. When the measurements were made with sufficient care, when using λ, 5890 or 5876, the results obtained agreed to within ±0.003 with the more accurate values obtained with the refractometer.

A number of check experiments, other than the microscopic observations, were carried out. The mean index of refraction of dibenzyl was calculated from the angle of minimum deviation of a prism formed by developed faces on crystals grown from solution. The observed values are

Line	*Prism*	*Total reflection*	*Immersion (microscope)*
5461	1.6334	1.6330	1.633
4358	1.6591		

Naturally developed faces of dibenzyl, β-naphthol dimethyl amine, and p bromo-chloro benzene gave results identical, to within experimental error, 1′, with values obtained from flat surfaces of these compounds prepared by melting.

The intermediate index was found by comparison of the limiting curves for several sections differently oriented with respect to the optical ellipsoid. It was casually noted that for a disproportionately large number of compounds a principal direction was normal to a cleavage surface. This is not unexpected since cleavage too depends upon the molecular arrangement within the crystals.

The data that we have obtained are summarized in Table III. It is probable that the absolute values of the refractive indices are not in error by as much as 0.0005 and the dispersions are perhaps somewhat more accurate. The measurements on liquids listed in the table are usually those reported by J. F. Eykman.[16] The values given for liquid naphthalene and p dibromobenzene are those of K. Auwers and A. Fruhling.[17] We have also included the results of K. Heydrich[18] on the crystalline dihydroxy derivatives of benzene.

The maximum refractive indices of diphenyl, naphthalene, and p dibromobenzene were not measured since they are greater than refractive index of Rohrbach's solution. The values of the optic axial angles were calculated for the various compounds for λ, 5890, 5876 or 5780. These calculated values can only be accepted as approximate since they are very sensitive to variations in the indices of refraction. Among the compounds examined $2V$ has been directly measured for benzoic acid only, which indeed was the first biaxial substance for which the optic orientation has been determined. The calculated and observed values of $2V$ for Na_D are 64° 24′ and 62° 37′,[19] respectively; the difference considerably exceeds our experimental error.

Completely refractivity data are listed for six compounds in Table III. The Lorenz-Lorentz expression: $(n^2-1)/(n^2+1)\cdot(\text{m.w.}/\rho)=\text{const.}$ was used for calculating the mole refractivities. In the case of the solid a mean index of refraction was calculated as

$$n=[(\alpha^2+\beta^2+\gamma^2)/3]^{\frac{1}{2}}\ ^{20}$$

and, for comparison with the liquid, was corrected for change in density upon melting. The refractivity of the liquid is, in all cases, slightly

[16] J. F. Eykman, *Recherches Refractometriques*, edited by A. F. Holleman, Haarlem (1919).

[17] K. Auwers and A. Fruhling, Ann. d. Chemie **422**, 160, 192 (1921).

[18] K. Heydrich, Zeits. f. Krist. **48**, 243 (1911).

[19] W. H. Miller, Trans. Cambridge Phil. Soc. **5**, 436 (1835).

[20] *Note:* The basis for this method of averaging rather than the use of the geometric or arithmetic mean will be discussed in the theoretical part of the present work.

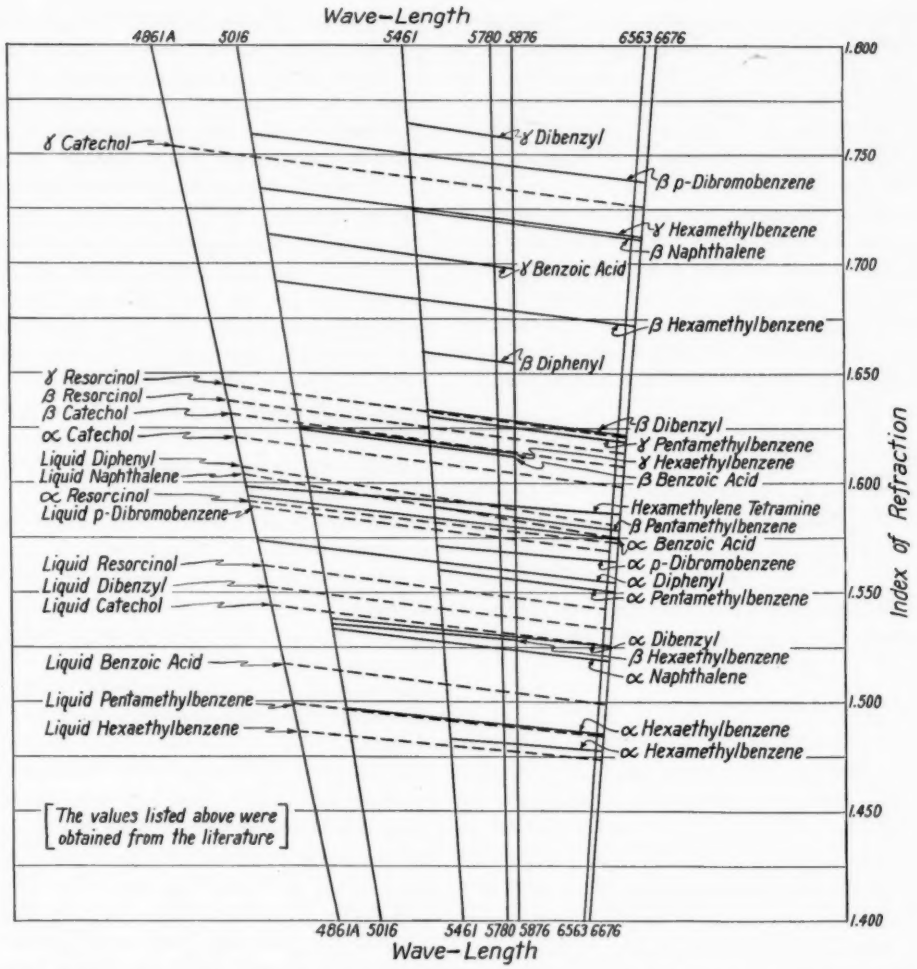

FIG. 1. Dispersions of the refractive indices for various aromatic compounds and hexamethylene tetramine.

greater than the average value obtained from the solid. A large discrepancy for hexaethylbenzene caused us to check carefully the values determined for that compound, but we were unable to find errors in our work. It might be suggested that Eykman's material was somewhat impure. In general these data bear out the assumption that the "apparent" anisotropies of the molecules are quite closely similar in the liquid and solid states.

Dispersion curves for the various compounds are shown in Fig. 1. The slopes of the curves for aromatic compounds are all closely similar and distinct from that of hexamethylene tetramine which was the only aliphatic compound examined. The substances have absorption bands in approximately the same region in the ultraviolet,[21] 2500–3000A while hexamethylene tetramine is probably transparent above 1800A.

The inherent molecular anisotropies of the aromatic compounds that were examined are all probably of the same magnitude. Birefringences of the crystal, however, show marked variations since their values are determined also by the

[21] Note for instance F. W. Klingstedt, Zeits. f. physik. Chemie **B20**, 125 (1933).

orientation of the molecules. The qualitative dependence of birefringence upon structure is perhaps best illustrated by a comparison of penta- and hexamethylbenzenes. In crystalline hexamethylbenzene molecules can be brought to superposition by translations alone,[14] thus a large birefringence is observed, 0.2395 for $\lambda = 5780$. Pentamethyl benzene, the structure of which is unknown, has a birefringence of 0.0695 and thus safely can be said to have at least two differently oriented molecules in its unit of structure.

Some values of the indices of refraction as recently determined by other workers are listed below for comparison with our parenthetically indicated ones:

Substance	αD	βD	γD
Naphthalene[22]	1.442 (1.5238)	1.775 (1.7182)	1.932 (>1.80)
Hexamethylbenzene[23]	1.5032 (1.4805)	1.7475 (1.6791)	1.8012 (1.7199)
Diphenyl[24]	1.554 (1.5598)	1.586 (1.6542)	1.647 (>1.90)

Casual observation with a microscope is sufficient to make apparent the errors in the previous work.

Abnormal Refractive Indices of Naphthalene

Some surfaces of naphthalene immediately after preparation, either by polishing or by melting, showed an extraordinary variation of the minimum refractive index as determined from the critical angle. Typical results for $\lambda 5780$ are:

Polished		*Melted*	
Time	Angle	Time	Angle
9:25	52° 34′	1:30	52° 38′
9:27	52° 36′	1:40	52° 39′
9:30	52° 39′	1:55	52° 40′
9:35	52° 42′		
9:50	52° 42′		

The maximum variation observed was from 52° 31′ to 52° 41′ for $\lambda 5780$ corresponding to a change of about 0.0035 in the refractive index. Sections parallel to the cleavage plane showed the most pronounced variations. The variations in critical angles for other sections were less, being unobservably small for some surfaces normal to the principal cleavage directions. The demarcation in the field of the telescope was equally sharp for all surfaces. The intermediate refractive index remained constant for all sections. The critical angle with the electric vector in the direction of the maximum refractive index was not observed since it was above the limit set by the Rohrback solution which was used as the contact liquid.

A tenable explanation for this behavior, developed in greater detail below, is that the orientations of the naphthalene molecules near the boundaries of the crystal are changed in the preparation of a surface. When the deforming force is removed the molecules slowly return to their equilibrium positions. The difference in behavior with section is perhaps accounted for by the differences in the orientations of the molecules relative to the prepared face.

The crystal structure of naphthalene has been determined by K. Banarjee.[25] The unit of structure contains two molecules; the space group is $P2_1/c$. The molecules have a center of symmetry and for the present purpose are brought to superposition by a glide reflection. One axis of the optical ellipsoid of the crystal thus approximately coincides with a principal direction of the molecule polarization ellipsoid, this direction being that of the maximum optical susceptibility which probably coincides with the long axis of the molecule. The long axes of the molecules are parallel in the glide plane, which is the plane of the optic axes, and are at an angle of 12°, in the obtuse angle β, to the crystallographic c axis which has been said to be approximately the obtuse bisectrix; they thus are at an angle of about 20° with the normal to the cleavage plane.

The sections that we have studied thus have the c axis either approximately in their planes or perpendicular to them. Our results suggest that the surface molecules are slightly rotated about their long axes, half clockwise and half counterclockwise with some decrease in density. Rotation alone would be expected to decrease the minimum refractive index and to increase the intermediate, while leaving the maximum unchanged. A decrease in density could further decrease the minimum, decrease the maximum, and return the intermediate to an apparently unchanged value.

[22] S. Bhagavantam, Proc. Roy. Soc. **A124**, 545 (1929).
[23] S. Bhagavantam, Proc. Roy. Soc. **A126**, 143 (1929).
[24] K. L. Narasimham, Indian J. Phys. **6**, 233 (1931).
[25] K. Banarjee, Nature **125**, 456 (1930); Indian J. Phys. **4**, 557 (1930).

An alternative explanation would be that the maximum index is not solely determined by the orientation of the molecules and that its limiting value is not necessarily a maximum one. In this case the maximum index of refraction could decrease as the minimum increased with the intermediate remaining constant.

Data are not here at hand for estimation of the minimum thickness of the modified layer. In the case of a polished glass surface the thickness[26] of a transition layer has been shown to be *ca.* 100A. It might be expected that the surface effect extends over the order of ten molecules down into the crystal. The actual effect could vary with depth and still give a sharp demarcation in the field of the telescope.

We are deeply indebted to Dr. H. E. Merwin of the Geophysical Laboratory, Carnegie Institution of Washington for many discussions on the optical properties of crystals and for material assistance most graciously given. Dr. F. G. Cottrell made many ingenious suggestions during the course of the work.

[26] See P. Drude, *Theory of Optics*, New York, 1929, p. 295.

Summary

Refractive indices and mean molecular refractivities have been determined for some organic compounds. Accurate methods have been devised for determining the densities of crystals and for the preparation of crystal surfaces suitable for use on the total reflectometer.

Freshly prepared surfaces of crystalline naphthalene have variable minimum refractive indices that after some time approach the same limit. The intermediate refractive indices of such surfaces are constant.

Studies in Refractive Index. Part IV*

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(Received June 10, 1933)

In this paper an account is given of an extension of the second method for determining refractive indices of liquids in thin films, previously described in Part I of this series. The apparatus was modified mechanically and optically and an air thermostat built to contain it. The critical angle of reflection from glass to liquid was determined for three normal fatty acids, undecylic, lauric and myristic, in the molten state. The surface layers of the liquid phase were observed to become suddenly birefringent within a narrow range of temperature immediately above the temperature of solidification, thus indicating orientation of the molecules of the molten acid to a depth of at least a wave-length or so of visible light.

THE DOUBLE REFRACTION OF INTERFACIAL LAYERS OF THE NORMAL ALIPHATIC ACIDS

Introduction

The second of the methods described in Part I of this series,[1] for the determination of refractive indices of liquids, offers a very convenient means of attacking the problem presented by those substances which are on the borderline between isotropic liquids and "liquid crystals." The phenomenon of anisotropy is directly connected with the elongated structure of the molecule. "Cybotaxis," or the parallel arrangement of molecules of some liquids in quickly changing groups large enough to be demonstrated by x-rays[2] but too small to show optical anisotropy, has its origin in the same elongated structure of the molecule. Not only this elongation but also a zig-zag form of the molecules has been demonstrated by Vorländer[3] to occur in many cases of anisotropic liquids.

The normal saturated aliphatic acids have precisely the long zig-zag molecules which may be expected to show anisotropy in the liquid state. Morrow[4] has found evidence for cybotaxis of the fatty acids and many other investigators have shown that these molecules are oriented in parallel fashion at interfaces, particularly if the second material is aqueous,[5] metallic,[6, 7] or is a glass.[8] This orientation was found by Trillat[6] to extend in the solidified acids to a depth of 200–300 molecules, i.e., over 5000A for molecules with 10–12 carbon atoms, and was believed to exist in the liquid state immediately prior to solidification. Such orientation, if it exists, while too small to be perceived under a polarizing microscope in the usual way of examining Lehman's anisotropic liquids,[9] should cause optical anisotropy sufficient for detection as birefringence of the interfacial layer.

In determining refractive index by critical angle methods it is known that there is a superficial wave in the second medium even at total reflection, and that the amplitude of this superficial wave falls off exponentially as the distance from the interface,[10, 11] as soon as the critical angle is exceeded by a very small amount. If the critical angle is determined by measuring the angle at which the reflection coefficient reaches unity, as in the second method described in Part I, it is clear that if the medium under examination is birefringent different values of the

* Parts I and II, reference 1; Part III, reference 11.

[1] A. M. Taylor and A. M. Glover, J.O.S.A. **23**, 206 (1933).

[2] G. W. Stewart and R. M. Morrow, Phys. Rev. **30**, 232 (1927).

[3] D. Vorländer, *Chemische Krystallographie der Flüssigkeiten*, Leipzig, 1924.

[4] R. M. Morrow, Phys. Rev. **31**, 10 (1928).

[5] N. K. Adam, *The Physics and Chemistry of Surfaces*, Oxford, 1930.

[6] J. J. Trillat, J. de Physique et le Radium **10**, 32 (1929).

[7] L. Tronstad, Trans. Faraday Soc. **29**, 502 (1933).

[8] J. J. Trillat, C. R. **188**, 555 (1929).

[9] D. Vorländer and W. Selke, Zeits. f. physik. Chemie **129**, 435 (1927).

[10] C. V. Raman, Trans. Opt. Soc. **28**, 149 (1927).

[11] A. M. Taylor and D. A. Durfee, J.O.S.A. **23**, 263 (1933).

critical angle will be found according to the direction of the electric vector. This will be true unless it should happen that the direction of propagation of the superficial wave should coincide with the optic axis of the doubly refracting medium at the interface.

If the molecules of the medium are oriented with respect to the interface, the optical anisotropy produced will most probably be such that the optic axis of the doubly refracting surface layer will be normal or approximately normal to the interface. If the incident light is plane polarized with the electric vector either in or perpendicular to the plane of incidence, any marked departure of the optic axis from normality will result in elliptical polarization of the reflected ray, as may be seen in an Abbe[12] crystal refractometer.

Apparatus

The method already described in Part I was used,[1] but the apparatus was somewhat modified to meet the new conditions. The optical arrangement is shown in Fig. 1. The source of light was a

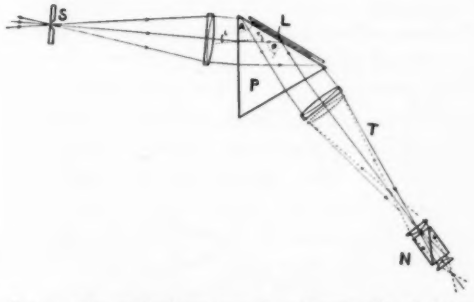

FIG. 1. The optical system; *S*, entrance slit of the collimator; *P*, prism; *L*, molten acid; *T*, tele-microscope; *N*, eyepiece and polarizing prism.

mercury arc having a Corning No. 401 filter and a didymium glass filter in order to isolate the green line of wave-length 5461A. The light after collimation was internally reflected in the prism *P* and entered the tele-microscope *T* which was focussed on the interface *L*. The eyepiece *N* contained a square ended Glan-Thompson prism which was rotatable, and the mount was provided with stops so that it was easy to set the analyzer to transmit light with the electric vector either parallel or perpendicular to the plane of incidence on the surface *L*.

As the prism *P* was rotated, the angle of incidence φ was altered, and the reflected rays were turned through twice the angle of rotation of the prism. To facilitate readings, a linkage was constructed as shown in Fig. 2, and this kept the tele-microscope always in the correct position as the spectrometer table was rotated.

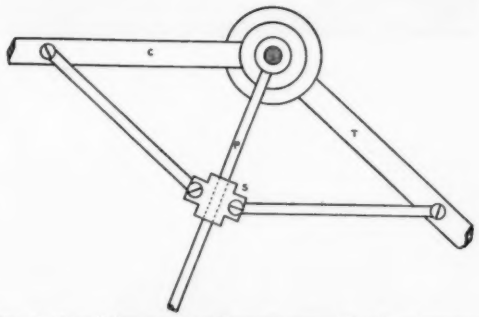

FIG. 2. The linkage; *C*, collimator arm; *T*, tele-microscope arm; *P*, prism table arm; *S*, sliding shackle.

Because it was expected that any observable birefringence of the surface layers would be restricted to a small temperature range immediately above the solidification point of the material to be examined, it was necessary to design a thermostat for the work. In order to avoid the expense of the optical flats requisite for a thermostatically controlled heating chamber which should enclose the prism only, it was decided to place the whole spectrometer in an air thermostat and to allow the eyepieces of the two telescopes and the collimator slit to project through the sides of the box. The apparatus is shown in Figs. 3 and 4. The thermostat was heated by two nichrome wire grids placed in front of the two fans and governed by a thermostat control mounted in the blast of air from the fans. The control, by means of a relay, shunted in or out a suitable ballast resistance, so that the rates of heating and cooling were approximately equal. A small spring on a shaft driven by the fan belt, continually tapped the thermostat control and so prevented any sticking of the

[12] P. Drude, *Theory of Optics*, p. 340.

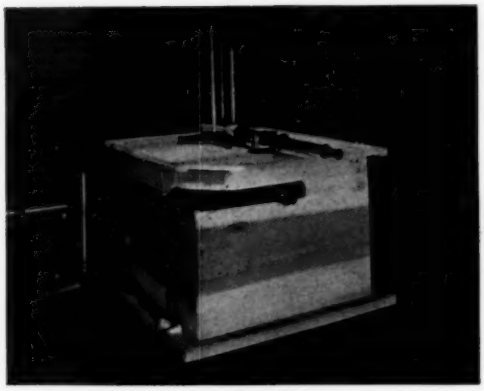

FIG. 3. The apparatus showing the observing telescopes, etc.

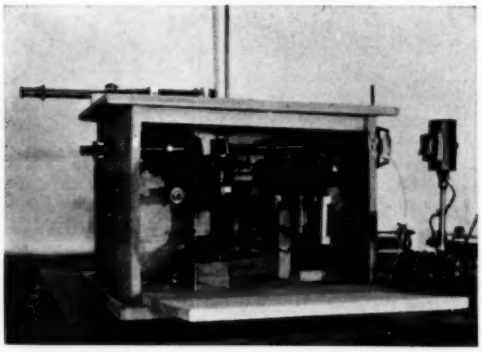

FIG. 4. The apparatus; the side of the thermostat is open and the fans, heating coils, etc., may be seen.

contacts. The temperature was read by a calibrated thermometer reading to 0.1°C, which was mounted so that the bulb was in contact with the top of the glass prism *P*. The temperature was usually constant to a tenth of a degree, and the range of the air thermostat was from room temperature up to about 65°C.

The circular scale on the spectrometer could be read to 20″ arc but this was insufficient for the purpose, and, because of the wooden case, inconvenient. Consequently the glass tube which carried the thermometer, and which was clamped in a bracket so as to coincide with the axis of rotation of the prism table was also made to carry a front silvered optical flat, 3 cm square. A telescope on top of the thermostat was used to read the image of a $\frac{1}{2}$ mm scale reflected in the mirror. The distance of the scale was about 260 cm and, therefore, 1 mm on the scale corresponded to 41″ of arc rotation of the mirror. The resolving power and magnification of the telescope were sufficient to enable readings to be estimated to tenths of a half millimeter division, and this meant that changes in setting of the prism table could be measured to 2″ arc. The prism table was moved by a fine adjustment screw turned by a knob outside the box.

Measurements

A flint glass prism of refractive index 1.625 for a wave-length of 5461A was cleaned with soap and water, soaked in chromic acid, and washed for ten minutes in several changes of distilled water, and dried with a clean chamois leather. A few small drops of the melted acid were then placed on the surface *L* of the prism (Fig. 1) and a clean microscope cover glass pressed into close contact. When the prism was in position the drops could be observed in the tele-microscope *T*; and if the angle of incidence on the glass-liquid interface was less than the critical angle the drops appeared darker than the surrounding field (glass-air reflection). Measurements were made of the critical angle by one of the two methods previously described.[1] The first of these was to turn the prism table slowly until the illumination of the drops appeared just equal to that of the surroundings. The second was to observe the Ketteler-Helmholtz interference bands and to turn the prism until the last of these disappeared. Both methods were used and seemed to give identical values for the critical angle.

After the temperature had been held constant for half an hour or more readings corresponding to the critical angles were made; after each observation the analyzing prism was turned counterclockwise through 90°. In this manner alternate readings were obtained for the electric vector horizontal and perpendicular to the plane of incidence. Provided the temperature remained constant, a set of ten pairs of readings were made. Occasionally, however, some chance fluctuation of the temperature would occur and so terminate the series; but if the set lacked only a few readings of the usual twenty the observations

were not rejected. The average value of the settings for both positions was tabulated and also the mean residuals. The difference between the settings for the two directions of the electric vector is a measure of the birefringence. It may be shown that

$$n_l = n_g \sin [A + \text{arc sin } \{(\sin i)/n_g\}],$$

where n_l is the refractive index of the liquid, n_g that of the glass, A is the angle of the prism, and i is the angle of incidence on the first surface, as in Fig. 1. By differentiation it is found that

$$\Delta n_l = \cos i\{\cos A - \sin A \sin i/(n_g^2 - \sin^2 i)^{\frac{1}{2}}\}\Delta i.$$

Because, for any one acid, i varies less than 30 minutes of arc over the whole range of observation, the coefficient of Δi may be considered constant. In Table I a sample set of readings is given. The value of Δi thus found from each set of twenty readings is then plotted against the temperature.

TABLE I. *Sample set of data for one point. Lauric acid.*

Temperature: Thermostat 42.0°–41.9°C. Room 25.8°C. Corrected temperature 42.1°C.

Electric vector perpendicular to the plane of incidence		Electric vector parallel to the plane of incidence	
Scale reading (cm)		Scale reading (cm)	
8.32	8.29	8.23	8.18
8.30	8.315	8.18	8.22
8.305	8.31	8.17	8.21
8.295	8.28	8.22	8.195
8.295	8.35	8.21	8.20
Average	8.306		8.202
Mean residual	±0.014		±0.017
Probable error	±0.0042		±0.0043

$\Delta s = 0.104$ $\Delta i = 42.6$ seconds

If the orientation in the interfacial layer is assumed to be approximately normal to the glass surface, the optic axis of this doubly refracting layer must be in the same direction. Consequently settings made with the electric vector in the plane of incidence depend upon the extraordinary index n_ϵ and those made with the electric vector perpendicular to this plane depend upon the ordinary index n_ω. With due regard to sign, therefore, $\Delta n_l = (n_\epsilon - n_\omega)$, which is the birefringence of the oriented layer. In the graphs which have been plotted of Δi, which is proportional to the birefringence of the various acids, points with different symbols belong to different runs. A run was considered to comprise all readings taken between complete isotropic liquefaction of a drop under observation, and its crystallization to the solid phase.

Undecylic acid $CH_3(CH_2)_9COOH$. The specimen available was rather impure, and it was, therefore, subjected to fractionation in vacuo in the molecular distillation apparatus[13] kindly placed at our disposal by Dr. K. C. D. Hickman of the Eastman Kodak Research Laboratory. The best fraction solidifying at 26.15°C was used. The birefringence is shown in Fig. 5. Although

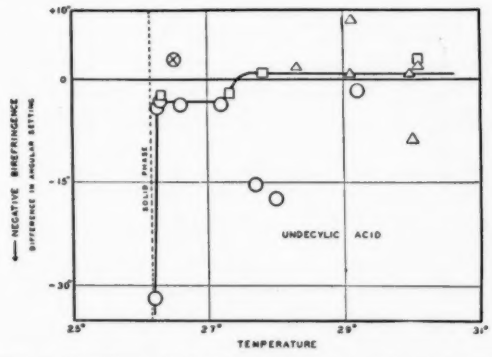

FIG. 5. Readings obtained in different experimental runs are indicated by different symbols.

there is a rather large scatter of the experimental points it may be seen that there is evidence of negative birefringence which sets in about 1.1°C above the solidification temperature.

Lauric acid $CH_3(CH_2)_{10}COOH$. The specimen solidified at 41.8°C, and was not fractionated. It showed pronounced anisotropy, which set in at 5.7°C above the solidification temperature, and which in this case indicated positive birefringence (Fig. 6).

Myristic acid $CH_3(CH_2)_{12}COOH$. The sample solidified at 52.1°C and was not fractionated. This acid behaved very similarly to lauric acid, but the anisotropy was not so marked, and the range was but 2.5°C above the solidification temperature. The sign of the birefringence was again positive (Fig. 7).

[13] K. C. D. Hickman and C. R. Sanford, J. Phys. Chem. **34**, 637 (1930).

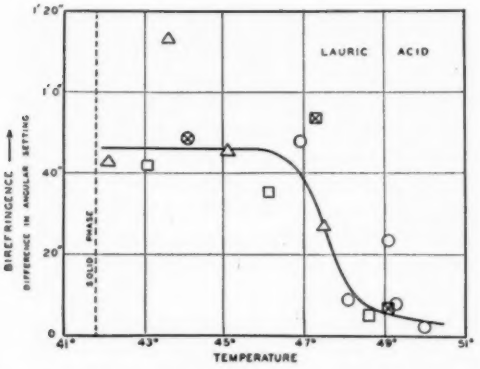

FIG. 6. Readings obtained in different experimental runs are indicated by different symbols.

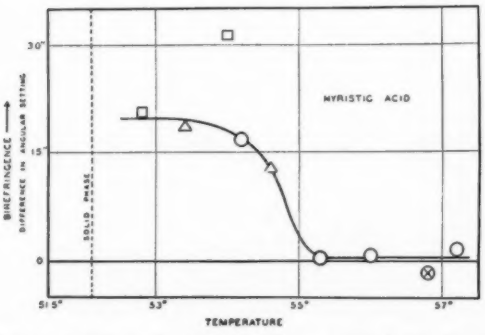

FIG. 7. Readings obtained in different experimental runs are indicated by different symbols.

Conclusion

The results for the liquid acids are collected in Table II. The values of the birefringence are markedly affected by the purity of the sample and it is unsafe to place too much weight on the numerical data. At the same time it is evident from the graphs that there is definite optical evidence not only of orientation of the molecules of these fatty acids at an interface between the liquid acid and glass, but also of the somewhat abrupt disappearance of the effect at a critical temperature not far removed from the melting point. It would appear, moreover that while the two acids having an even number of carbon atoms give rise to surface layers of positive birefringence, undecylic acid having an odd number of carbon atoms shows weakly negative birefringence.

TABLE II.

Acid	Number of C atoms	Solidification temperature	Range of anisotropy	Δi in seconds of arc	Birefringence of the anisotropic layer
Undecylic	11	26.15°C	1.1°C	−3″	−0.000007
Lauric	12	41.8°C	5.7°C	+46″	+0.000104
Myristic	14	52.1°C	2.5°C	+20″	+0.000051

As has already been indicated evidence for the orientation of molecules in surface layers has been collected by many other workers. The present method shows that this orientation may be detected optically by the double refraction produced, and the fact that such observation is possible implies that the oriented layer must be of thickness comparable to or greater than a wavelength of visible light; i.e., to a depth of at least 200 molecules. The abrupt transition from isotropic to anisotropic liquid at a definite temperature may well indicate the appearance of a new phase, and that the orientation is not confined merely to the surface layers, but is possibly distributed through the bulk of the liquid.

It is hoped to continue this work in several directions. Not merely the birefringence but also the magnitudes of the refractive indices will be determined. Tridecylic, pentadecylic and palmitic acids will be studied and the method will be applied to other substances besides the aliphatic acids. The light reflected at the critical angle will be examined for elliptic polarization in an endeavor to find the angle at which the molecules are oriented with respect to the interface.

In conclusion our grateful acknowledgments must be made to Professor E. K. Rideal at whose suggestion this present extension of the work was attempted, and in whose laboratory at Cambridge, England, a few preliminary trials were made by one of us (A.M.T.) last summer.

The Aberrations of the Concave Grating at Large Angles of Incidence

I. S. BOWEN, *California Institute of Technology*

(Received June 24, 1933)

Mack, Stehn and Edlen have treated the aberrations of a concave grating at large angles of incidence for the case in which both slit and plate are on the Rowland circle. The present paper shows that, by allowing minor departures from this position, it is possible to reduce the aberration to one-fourth of the value found by them. This increases the optimum grating size and maximum resolving power by a factor of $2^{\frac{1}{2}}$. Certain conditions are discussed under which an even greater increase in the size of the grating is desirable.

MACK,[1] Stehn and Edlen have given a very elegant and rigorous treatment of theory of the concave grating when used at large angles of incidence. This study indicated that the concave grating has a maximum resolving power which is attained when the grating has a certain optimum width. In their treatment they assume that the slit and plate were placed exactly on the Rowland circle. This, of course, fixes the plate at the focus of the rays reflected at the center of the grating. In general, however, when an optical system has aberrations of the type found by these authors, the plane where the sharpest image is formed is displaced from the plane where the central rays are brought to a focus.

The theory of Mack, Stehn and Edlen may be extended to include cases in which either or both the slit or plate are slightly displaced from the Rowland circle by generalizing the values of their r and r' to

$$r=(\rho+\Delta)\cos\theta;\quad r'=(\rho+\delta)\cos\theta',$$

where Δ and δ are small quantities. The other symbols have the same significance as in their paper. If we neglect powers of Δ/ρ, δ/ρ and y/ρ higher than the fourth this yields for the length of the optical path

$$\overline{AP}+\overline{PA'}=r+r'-(\sin\theta+\sin\theta')y-(\Delta\cos\theta+\delta\cos\theta'-\Delta^2[\cos\theta]/\rho-\delta^2[\cos\theta']/\rho)y^2/2\rho^2$$
$$-(\Delta\sin\theta+\delta\sin\theta')y^3/2\rho^3+(\sin\theta\tan\theta+\sin\theta'\tan\theta')y^4/8\rho^3. \quad (1)$$

Since in an ideal grating the optical path is $r+r'-(\sin\theta+\sin\theta')y$ where $\sin\theta+\sin\theta'=m\lambda/\sigma$, the amount of the aberration for the spherical concave grating is given by

$$\epsilon=-([\Delta-\Delta^2/\rho]\cos\theta+[\delta-\delta^2/\rho]\cos\theta')y^2/2\rho^2-(\Delta\sin\theta+\delta\sin\theta')y^3/2\rho^3$$
$$+(\sin\theta\tan\theta+\sin\theta'\tan\theta')y^4/8\rho^3. \quad (2)$$

When $\Delta=\delta=0$ the coefficients of the y^2 and y^3 terms vanish and the aberration reduces to the case treated by Mack, Stehn and Edlen.

Since both Δ and δ are arbitrary, we may vary the coefficients of y^2 and y^3 at will and use these terms to decrease the aberration caused by the y^4 term. Obviously the y^3 term cannot simultaneously be used to decrease the aberration of the fourth power term for both positive and negative values of y and consequently its coefficient should be made zero. On the other hand the y^2 term may be used to counteract the y^4 term for both positive and negative values of y. Thus a simple calculation shows that over the range from $y=-Y$ to $+Y$ the maximum value of the aberration is cut to one-fourth the value which it has when the y^4 term alone is present, if the coefficient of the y^2 term is made equal to $-Y^2$

[1] Mack, Stehn and Edlen, J.O.S.A. **22**, 245 (1932). Mack and Stehn, J.O.S.A. **23**, 184 (1933).

times the coefficient of the y^4 term. Conversely, it is possible by the same process to keep the aberration at all points below a certain fixed value ϵ' over a range of y, $2^{\frac{1}{4}}$ times as great as when the y^4 term alone is present.

As a first approximation we may apply this fact to the determination of the optimum grating size using the simplified criteria that the grating be as wide as possible consistent with keeping the aberration at all points less than a certain fraction of a wave-length, say, one-fourth. It is then at once evident that when the plate is placed in the most favorable position slightly off the Rowland circle, the optimum size of the grating is $2^{\frac{1}{4}}$ times as wide as when slit and plate are both restricted to the Rowland circle as was assumed by Mack, Stehn and Edlen.

A rigorous deduction, based on a graphical calculation of diffraction patterns for the two cases when the plate is on the Rowland circle and when it is slightly displaced to its most favorable position yields, within the limits of accuracy of the calculation, the same ratio, i.e., $2^{\frac{1}{4}}$. In each case the optimum grating size is a few percent larger than that given by the simplified criteria.

This gives for the optimum grating size

$$2Y_{\text{opt}} = 3.55[\lambda\rho^3/(\tan\theta\sin\theta+\tan\theta'\sin\theta')]^{\frac{1}{4}}, \quad (3)$$

where ρ is the radius of curvature of the grating, θ the angle of incidence and θ' the angle of diffraction. When this is applied to the same examples treated by Mack, Stehn and Edlen in their first table we obtain the values given in our Table I.

TABLE I. *Values of grating width ($2Y_{\text{opt}}$ in cm) for maximum resolving power (1 meter grating).*

	$m/\sigma = 6000$ cm^{-1}				$m/\sigma = 24{,}000$ cm^{-1}			
	$\lambda = 10$	100	1000	5000	10	100	1000	5000
$\theta = 45$	1.8	3.3	6.0	9.7	1.8	3.3	6.4	9.5
80	1.1	2.0	3.8	6.0	1.1	2.1	4.0	6.1
88	0.75	1.4	2.7	4.1	0.79	1.5	2.7	4.1

This change in the position of the plate to the point of sharpest focus also increases the maximum resolving power by about the same ratio, i.e., $2^{\frac{1}{4}}$. In some cases this makes the widths of the spectral lines considerably narrower than the limit of resolution of the photographic plates. In these cases an even wider grating is advisable because of the greater intensity obtained. The optimum size of the grating is then the maximum size for which all the light from the grating can be made to fall in a band approximately equal to the limit of resolution of the plate.

For the treatment of cases where this criteria holds it is, as a first approximation, permissible to use geometrical optics. In tracing the path of the rays diffracted from various parts of the grating it is necessary to find the value of δ corresponding to the point where the ray diffracted at any point y on the grating intersects the ray from the center of the grating. This may be determined by setting the derivative of ϵ (Eq. (2)) with respect to y equal to zero and solving for δ. This gives, on making the usual approximations,

$$\delta = \frac{(\sin\theta\tan\theta+\sin\theta'\tan\theta')y^2/2\rho-3\Delta\,[\sin\theta]y/2\rho-\Delta\cos\theta+\Delta^2\,[\cos\theta]/\rho}{\cos\theta'(1+3\,[\tan\theta']y/2\rho)}+\frac{\Delta^2\cos^2\theta}{\rho\cos^2\theta'}. \quad (4)$$

The distance d from the Rowland circle to this intersection measured along the central ray is then, when the expression for δ is expanded and powers higher than the second in Δ and y are neglected

$$d = \delta\cos\theta' = (\sin\theta\tan\theta+\sin\theta'\tan\theta')y^2/2\rho-3\Delta\,[\sin\theta]y/2\rho+3\cos\theta\,[\tan\theta']\Delta y/2\rho$$
$$+\Delta^2\,[\cos\theta]/\rho-\Delta\cos\theta+\Delta^2\,[\cos^2\theta]/\rho\cos\theta'. \quad (5)$$

This is of the form

$$d = Ay^2/\rho^2+By/\rho+C,$$

where y/ρ is approximately equal to the tangent of the angle between the central ray and the ray under consideration. Since the y/ρ term introduces a dissymmetry between the two sides of the pattern we shall in general wish to eliminate it by setting B and therefore Δ equal to zero. For certain exceptions see the next to the last paragraph.

For "spherical aberration" of this type, in which the difference in focal length between any

FIG. 1. Nonsymmetrical arrangement of rays for the case that the coefficient, B, of the y term is not equal to zero.

ray and the central ray is equal to A times the square of the slope of the ray, the simple theory of caustics shows that the position of the sharpest image is at a distance $3AY^2/4\rho^2$ from the focal point for central rays. $2Y$ is the total width of the grating. The width of this sharpest image is $b=AY^3/2\rho^3$. This is just one-fourth of the width of the image that is formed at the plane where the rays from the center of the grating are brought to a focus. Since the angle of incidence of the central ray on the photographic plate is θ' the width of the line on the plate is

$$c=b/\cos\theta'=\frac{(\sin\theta\tan\theta+\sin\theta'\tan\theta')y^3}{4\rho^2\cos\theta'}.$$

Or if the limit of resolution of the plate is c then the optimum grating width is

$$2Y=2\left[\frac{4c\rho^2\cos\theta'}{\sin\theta\tan\theta+\sin\theta'\tan\theta'}\right]^{\frac{1}{3}}.$$

If we set $c=20\mu$ we obtain the values given in Table II. In general, if the maximum intensity is desired, it is advisable to use the widths called for in Table II when they are larger than those in Table I.

TABLE II. *Values of grating width (in cm) for an image width of 20μ (1 meter grating).*

	$m/\sigma=6000$ cm^{-1}				$m/\sigma=24{,}000$ cm^{-1}			
	$\lambda=10$	100	1000	5000	10	100	1000	5000
$\theta=45$	6.8	6.9	7.3	8.7	6.9	7.0	8.4	8.3
80	2.2	2.3	3.1	4.2	2.2	2.7	4.1	4.8
88	0.86	1.3	1.9	2.5	1.1	1.6	2.4	2.8

As mentioned above, if B the coefficient of the y/ρ term is not equal to zero, the rays near the focal point have a nonsymmetrical arrangement such as is shown in Fig. 1. For a photographic plate placed normal to the central ray this dissymmetry obviously decreases the resolving power. On the other hand, if the plate is tilted to give a high angle of incidence, i.e., the plate is placed in the position indicated by the dotted line in Fig. 1, the width of the image on the plate may be materially decreased by the introduction of the proper amount of dissymmetry. In general, however, the gain in definition obtained by the introduction of this dissymmetry is appreciable only when the angle between the extreme rays of the incident beam is comparable with the angle between the incident ray and the plane of the plate. As this rarely, if ever, occurs even in a grazing incidence spectrograph we may safely operate with the condition that B vanishes i.e., that $\Delta=0$ and the slit lies on the Rowland circle.

If the slit lies on the Rowland circle the focus for central rays also lies on the same circle. The point for sharpest focus of the rays from a finite grating, however, is displaced by a very small amount, usually much less than a millimeter, from the Rowland circle. Because of the smallness of this displacement the only practical method of giving the plate the proper displacement is by following the usual practice of adjusting photographically for the position of sharpest focus. Since the amount of this displacement varies rapidly with the width of the grating all adjustments should be made with the grating stopped to the width it is eventually to be used.

The Photographic Reciprocity Law Failure for Radiations of Different Wave-Length

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INTRODUCTION

THE object of this experimental work was to investigate the general manner in which the photographic reciprocity law failure varies for radiations of different wave-length. The method which has been followed generally by other experimenters[1] in this field has made use of a spectrograph, the variations in intensity being accomplished by altering the intensity upon the entrance slit of the spectrograph in a suitable manner. With the ordinary spectrograph and light source it is impossible to obtain values above optimal intensity for the photographic emulsion. Yet, intensities above optimal are essential to a complete study of the phenomenon of reciprocity law failure. Such high intensities may be obtainable with a high aperture spectrograph when used with an extremely high intensity light source, such as a high intensity carbon arc. However, to avoid the expense and attendant complications of such a system in this first survey of the field, it was decided to use an ordinary time scale sensitometer for making the exposures and a mercury arc, filtered so as to give only certain, strong, characteristic lines of this arc, as a source of monochromatic radiation. It was found possible, by a careful choice of filters, to isolate practically any of the strong lines from this source. The strong lines emitted in the spectrum of the mercury arc are quite uniformly spaced over the region of photographic sensitivity, thus making this source a particularly desirable one for this work. Another feature which makes this type of light source well suited to this work is its unusually steady intensity under the conditions of controlled voltage, constant ventilation, and continuous operation, all of which were obtained in these experiments.

For a review of the subject of reciprocity law failure, the reader is referred to former papers[2] on this subject published by members of this laboratory.

EXPERIMENTAL PROCEDURE AND RESULTS

All exposures in this work were made on the reciprocity sensitometer which has been used in the previous work on reciprocity law failure carried out in this laboratory. This instrument has been fully described in a paper by L. A. Jones.[3] The arrangement of apparatus in this work was the same as that used in former experiments and described in a former paper.[4] Exposures were made in the same manner as in this former work and the reader is referred to the above paper for a detailed description of the method employed. The intensity of the exposing radiation was varied by changing the distance from emulsion to light source and comparison exposures were in all cases made on a single four by five inch plate or film by means of a series of dark slides containing slots cut at different positions.

The arrangement of the light source and lamp house used in the present work is illustrated in the diagram of Fig. 1. This diagram shows a cross-sectional view of the lamp house with the horizontal type of mercury arc in place. The ground glass diffusing screen shown at (*C*) acted as the source. To vary the intensity of illumination, the lamp house was moved along the twelve meter track extending out from the sensitometer, the intensity falling off inversely as the square of the distance. In cases where a greater range of intensity variation was desired than that allowed by the length of the lamp track, the diaphragm (*B*) was changed to a smaller size. This procedure rendered the lamp track again available for the small step intensity changes necessary in obtaining the reciprocity curves.

The filters used for isolating the various lines of the mercury arc are listed in Table I. The wave-

* Communication No. 523, Eastman Kodak Research Laboratories.

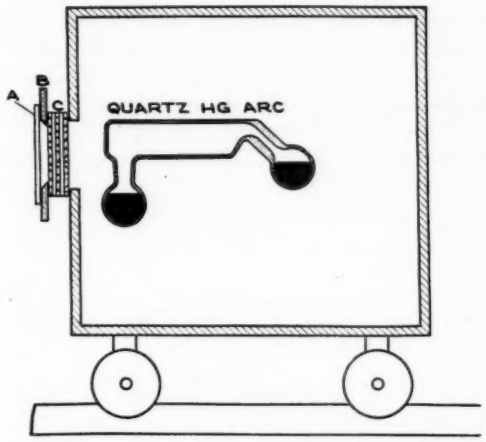

FIG. 1. Lamp house. *A*, filter, *B*, diaphragm, *C*, three ply ground glass.

TABLE I.

Line	Filter
3650A	Wratten No. 18A+1 cm 25% sol. $CuSO_4$
4050	Corning No. 8
4360	Corning No. 7.1
4916	Wratten No. 75 (2 ply)
5460	Wratten No. 77A+No. 58
6910	Wratten No. 70+No. 16

length of the spectral line transmitted by each is shown opposite the filter. These filters were first chosen by noting from diagrams their characteristic transmission properties, and were then tested visually in combination with the mercury arc by means of a visual spectroscope. Finally, to determine the photographic purity of the radiation obtained with each of the filter combinations, spectrograms were made on a quartz spectrograph with the filtered mercury arc as light source. These spectrograms showed that a pure monochromatic source was not obtained with all of the filter combinations employed. It is, generally speaking, impossible to segregate very closely neighboring spectral lines by means of glass or gelatin absorption filters. This was the case for the λ4050–80A lines and the λ6720–6910A lines used in these experiments. However, the above pairs of lines were regarded as monochromatic sources, and it is not believed that the experimental results have been invalidated in any way by this procedure. For convenience of reference, these pairs of lines will hereafter be referred to by the wave-lengths of only their stronger components, namely λ4050A and λ6910A, respectively.

Development was carried out in the D-90 developer given by the following formula:

A	Sodium bisulfite	17 g
	Pyro	20 g
	Sodium sulfite	70 g
	Water to make	1 l
B	Sodium carbonate	75 g
	Potassium bromide	1 g
	Water to make	1 l

The strips were brush developed for a period of four minutes at a temperature of 68°F.

Curves showing the extent of the failure of the photographic reciprocity law for radiations of different wave-length are shown in Figs. 2 and 3. These curves exhibit the variations in the logarithm of exposure required to produce unit density as a function of the logarithm of intensity. The curves of Fig. 2 are for a high speed blue sensitive emulsion, and the curves of Fig. 3 are for a high speed panchromatic emulsion. Hereafter these emulsions will be referred to ase mulsions I and II, respectively. The 45-degree lines placed on these diagrams are lines of constant times of exposure and were inserted for convenience of reference. That these lines are constant time lines can be readily verified by the following argument. Ordinates on the reciprocity diagram represent log It values, while the abscissa represent log I values. By formal analogy with the equation,

$$y = x + \text{constant}, \qquad (1)$$

which is the equation of a straight line of unit slope in terms of cartesian coordinates, it is readily seen that the equation,

$$\log It = \log I + \log t, \qquad (2)$$

represents a straight line of unit slope on the reciprocity diagram providing log t is constant.

The reciprocity curves of Figs. 2 and 3 were plotted in terms of absolute units of intensity and exposure using the units ergs/cm²/sec. and ergs/cm², respectively. The intensity was not

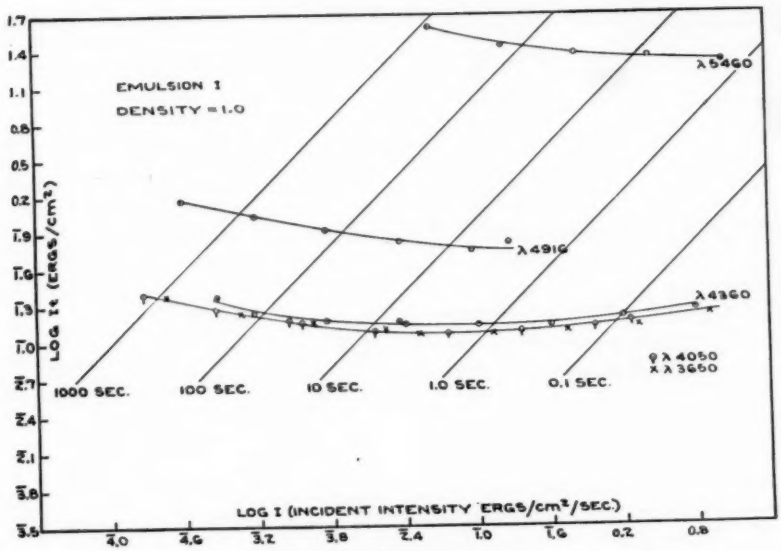

FIG. 2. Reciprocity curves.

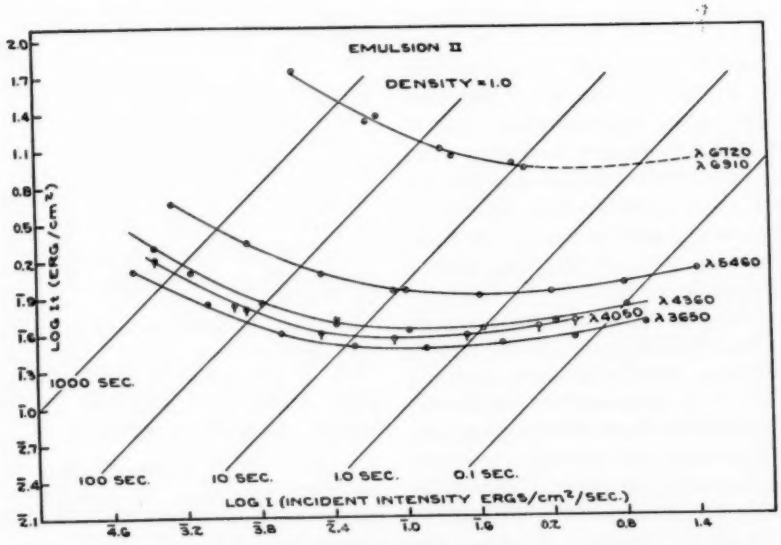

FIG. 3. Reciprocity curves.

measured directly for each spectral line used in these exposures. The procedure adopted consisted in the measurement of the energy per square cm per second radiated in the λ4360A line, and then by reference to the relative spectral energy curves, Fig. 4, the reciprocity

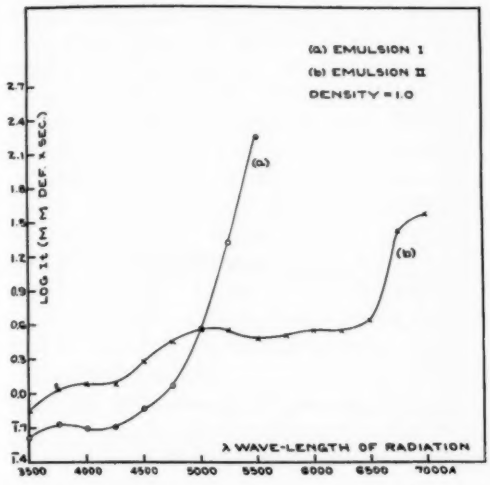

FIG. 4. Relative spectral energy curves.

curves for the other wave-length radiations were placed in their correct positions relative to that for the λ4360A line. In placing these reciprocity curves, particular care was taken to place the curves correctly according to the constant time lines. In this way, any error made in the intensity determinations only shifts the entire curve along the constant time lines. Also in placing these curves, account was taken of differences in exposure arising from the reciprocity law failure introduced by the variation of intensity along the spectral energy curve. This was accomplished by noting the times of exposures of points along the spectral energy curves and correlating these with points of the same exposure time on the reciprocity curves, when placing these curves on the reciprocity diagram.

The spectral energy curves were derived from exposures made on a monochromatic spectral sensitometer. The values of the ordinates of these curves, Fig. 4, show the relative quantities of energy required to produce unit density, as a function of wave-length for a constant development time. It should be added that the development conditions for the spectral energy measurements were identical with those for the reciprocity exposures.

The absolute value of energy of the λ4360A line radiated from the light source, was measured by means of a calibrated thermopile. This thermopile was calibrated by means of a Hefner amyl acetate lamp according to a method given by Coblentz.[5] For details of the experimental procedure in the calibration of this thermopile and the energy measurements of the λ4360A line, the reader is referred to a former paper[4] in which this work was described.

An examination of the reciprocity diagram, Figs. 2 and 3, shows that the reciprocity curves for the radiations of different wave-length are parallel in the direction of the 45 degree lines of constant time. That is, the intercept, measured along the constant time lines between any pair of curves, remains constant throughout the length of the curves. Though data are here given for only two emulsions, this result has been confirmed for two other emulsions of different characteristics. It is therefore believed that this result is a general one for all emulsions. Because of the parallelism of the reciprocity curves in the direction of the constant time lines, it appeared desirable to exhibit these same data by curves showing the relation between log $I \cdot t$ and log t. Curves on such a diagram being parallel vertically should portray more effectively the equality in shape of the reciprocity curves for different wave-lengths. The curves of Figs. 5 and 6 were plotted in this manner, and it is seen that they are parallel in the predicted manner for radiations of different wave-length.

The experimental fact manifested by the parallelism of the reciprocity curves for different wave-length radiations has a bearing upon the subject of photographic tone reproduction of colored objects. For example, let it be assumed that two objects of different color are photographed simultaneously at a particular level of illumination and that the relative brightness of the two objects is such as to produce equal densities on the photographic emulsion. If now the level of illumination on both objects is changed to any other value (the relative brightness of the two objects remaining the same) the

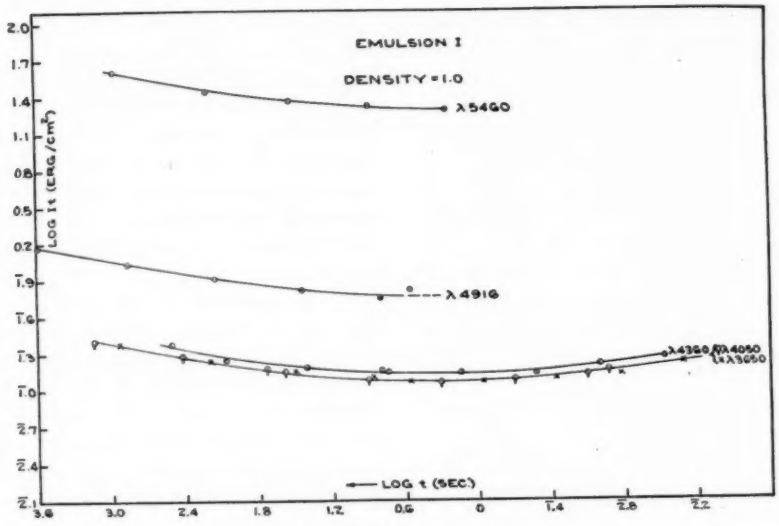

FIG. 5. Reciprocity curves.

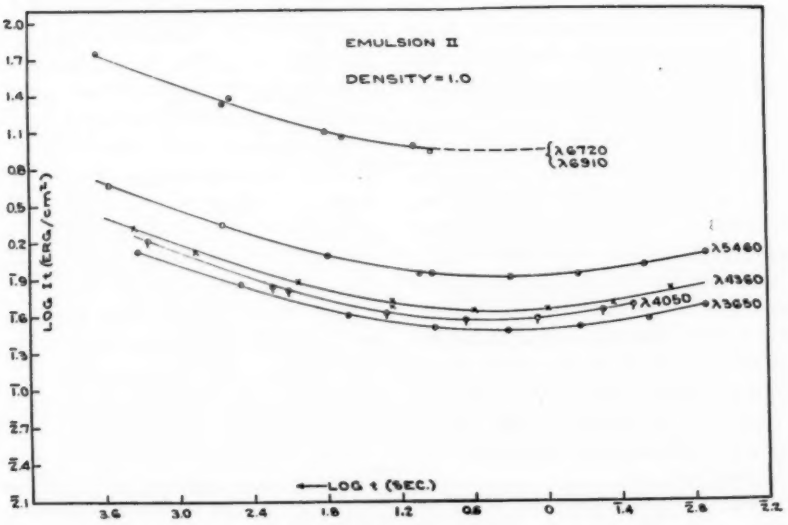

FIG. 6. Reciprocity curves.

objects will again produce equal densities when photographed at the new level of illumination. If the reciprocity law failure were not identical for the various wave-length radiations, this would not be true. Thus the above experimental results show that the relative values of photographic tone for different colors are maintained over any range of intensity values.

Another aspect of the foregoing experimental results is their bearing upon the question of latent image formation. The parallelism of the reciprocity curves suggests that the corresponding constant time points on these curves represent points of equal rates of utilization of radiation. This equality of rates of utilization of radiation of different wave-length might correspond to equal rates of reception of energy or equal rates of reception of quanta. The two are not the same for different wave-length radiations due to the fact that the energy of a quantum is inversely proportional to its wave-length. It was believed that the above suggestion could be tested by an experiment based on the previously demonstrated experimental fact[4] that an intermittent and continuous exposure of the same average intensity produces the same photographic densities at and above a certain critical frequency of flash, f_c. At the time of this previous experiment, the hypothesis was made that the critical frequency, f_c, corresponded to the value at which on the average there was one effective quantum received per grain per flash of the intermittent exposure. The meaning of this hypothesis is most readily conveyed through the equation

$$f_c = \rho I_{av}, \tag{3}$$

which was given in the presentation of this earlier work. In this equation, I_{av} represents the average number of quanta incident per sq. cm per sec. during exposure and ρ is a constant (with respect to intensity) to be identified with the mean effective receptor area on the photographic grain. In the previous experiment only light of wave-length 4360A was used, and the calculated values of the receptor area ρ in that case were found to be of the order of magnitude, in size, of the area of the entire photographic grain. It was assumed in that case that rate of utilization of radiation corresponded to the rate of reception of quanta. In an exposure to longer wave-length radiation, however, it is possible that rate of utilization might correspond to the rate of reception of units of energy (equal in magnitude to that of shorter wave-length quanta) and thus to the rate of reception of pairs, trios, etc., of quanta.

Regardless of the mechanism assumed, however, it is believed that the critical frequency, f_c, measures the rate at which discrete photochemical processes take place during exposure, and it was deemed worth while to determine this quantity for several radiations of widely different wave-length. Accordingly, an experiment of this type was carried out using the emulsion II. This emulsion was chosen because of its wide range of spectral sensitivity and its large reciprocity law failure at low intensities, the former allowing for a wide difference in wave-length of the exposing radiation, and the latter insuring a relatively large degree of accuracy in the determination of f_c. Radiations of wave-length 3650A, 5460A, and 6910A were selected for this experiment as these lines are evenly spaced over a wide range of wave-lengths. Preliminary experiments were performed to determine the magnitude of incident intensity required in the case of each radiation to produce unit density in the same exposure time. The intermittent exposures were then made with a sector disk of ratio 1 : 4 (light to total period) in the exposing light beam. The sector was rotated during each exposure, the speed increasing by definite steps for successive exposures. This was continued until a value of frequency well past the critical value f_c was reached. The results of this experiment are illustrated graphically in Fig. 7. The ordinates represent the logarithm of exposure required to produce a constant density of unity at the various frequencies. It is seen that the values of the critical frequencies, f_c, for the three different wave-length radiations are approximately equal to unity and agree with one another within the limits of experimental error. The error in the determination of the relative values of f_c for the different cases is probably as great as a factor of two. However, considering the fact that the intensity values of the exposures to the radiations of wave-length 3650A and wave-length 6910A were in the ratio 1 : 32 in terms of energy (and

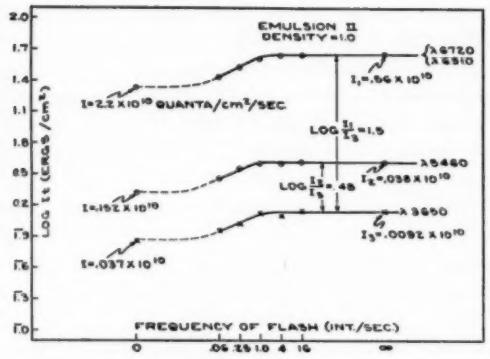

FIG. 7. Critical frequency of flash.

approximately 1 : 64 in terms of quanta) it is believed that the close agreement found between the values of f_c, signifies that the rates of utilization of radiation by the photographic grain is identical for different wave-lengths. Whether this means equal rates of reception of quanta or equal rates of reception of definite units of energy for the different wave-length radiations, this experiment is incapable of deciding. If the function of a sensitizer molecule is to collect energy through the absorption of two or more long wave-length quanta and then through collision or other similar mechanism transmit this integrated energy as a unit for the performance of a discrete photochemical process, then the critical frequency, f_c, might correspond to the value at which two, three, or more quanta of the long wave-length radiation were received per flash by a photographic grain. If this is true, the critical frequencies for the three different radiations could be equal though the number of quanta required for the exposure of a grain in the different cases might be different.

It is of interest to calculate the effective receptor area, ρ, on the photographic grain for the exposures to the radiations of different wave-length. For the λ3650A radiation, the value of ρ is found to be

$$\rho = f_c / I_{av} = 1.1\mu^2$$

in good agreement with the size of the larger grains of this emulsion. For radiation of this wave-length, it seems logical to conclude that the entire photographic grain acts as the receptor of the quanta, the developable centers being built up by a secondary (chemical, physical, or chemico-physical) process. For exposures to the λ5460A radiation, the value of ρ comes out to be

$$\rho = f_c / I_{av} = 0.3\mu^2,$$

a smaller area by a factor of three than in the previous case. For the case of the λ6910A radiation, the calculated value of ρ is found to be $0.02\mu^2$, only a minute fraction of the area of the photographic grain. It is to be borne in mind, however, that this exposure is an extreme case, as the radiation employed is practically at the long wave-length limit of sensitivity of the emulsion. From the foregoing results, it might be concluded that the variation in the size of the effective receptor area ρ accounts for (or is in direct agreement with) the variation of emulsion sensitivity with wave-length. The great increase in incident intensity required in the case of the long wave-length radiation would then be interpreted as necessary in order that an equal number of effective hits would be scored in the same length of time with the long wave-length radiation as with the radiation of wave-lengths 3650 and 5460A.

The apparent nondependence of the critical frequency, f_c, upon the wave-length of exposing radiation (Fig. 7), has been interpreted to mean that the rates of utilization of radiation, in exposures of equal time and density, are the same for radiations of all wave-length. Whether this rate of utilization agrees with the rate of reception of quanta or with the rate of reception of definite units of energy, the present experiment is incapable of deciding. It is believed, however, that f_c measures the rate at which some kind of discrete processes take place in the photographic grain during reception of the light. The equality of the values of f_c found for different wave-lengths, is believed to support the general thesis that the photochemical reaction taking place in the formation of the latent image is the same for radiations of all wave-lengths.

In conclusion, it is a pleasure to thank Mr. George Silberstein for making the spectral energy curves on the emulsions used in this work, and Mr. E. E. Richardson for making the spectrograms of the mercury arc.

Summary

1. Measurements of the reciprocity law failure were made on two types of emulsions, one a high speed blue sensitive and the other a high speed panchromatic emulsion, for radiations of various wave-lengths.

2. The reciprocity curves for the radiations of different wave-length were found to be identical in shape when compared in such a way that points of equal times of exposure coincided.

3. The equality in shape of the reciprocity curves for different wave-length radiations is interpreted as meaning that points of equal exposure time on the reciprocity curves correspond to conditions of equal rates of photochemical activity of the exposing radiation.

4. Determinations of the critical frequency, f_c, at which an intermittent and continuous exposure of the same average intensity produce the same density, were made for three radiations of widely varying wave-length. The equality of the values of f_c found in the three cases is believed to be evidence that the rates of the discrete photochemical processes, in exposures of equal time and density, are the same for radiations of any wave-length.

Bibliography

1. B. O'Brien, *Photographic Spectral Energy Measurements with a Spiral Aperture Disk*, Phys. Rev. **33**, 640 (1929).

B. O'Brien and E. Dickerman, *Intermittent Exposure in Photographic Spectrophotometry over Wide Intensity Ranges*, Phys. Rev. **37**, 471 (1931).

B. O'Brien and V. L. Parks, *Photographic Reciprocity and Intermittency Defects Near the Long Wave-Length Limit of Plate Sensitivity*, Phys. Rev. **41**, 387 (1932).

A. E. Weber, *Über die Anwendung des rotierenden Sektors zur photographischen Photometrie*, Ann. d. Physik **45**, 801 (1914).

F. Eckert and R. Pummerer, *Photographische Spektralphotometrie der Absorpionspektren um Farbstoffen*, Zeits. f. physik. Chemie **87**, 605 (1914).

K. S. Gibson, H. J. McNicholas, E. P. T. Tyndall, M. K. Frehafer and W. E. Mathewson, *The Spectral Transmissive Properties of Dyes*, Bur. Stand. Sci. Pap. **18**, No. 440, 121 (1923).

F. Twyman and F. Simeon, *The Logarithmic Wedge Sector and Its Use in Quantitative Spectrum Analysis*, Trans. Opt. Soc. (London) **31**, 169 (1929–30).

F. Twyman and A. Harvey, *The Validity of the Schwarzschild Relation as Applied to the Use of the Logarithmic Sector*, Trans. Opt. Soc. (London) **33**, 1 (1931–32).

C. E. Weinland, *The Intermittency Effect in Photographic Exposure*, J. Opt. Soc. Am. **15**, 337 (1927).

H. E. Howe, *On a Modification of the Hilger Sector Photometer Method for Measuring Ultraviolet Absorption and Its Application in the Case of Certain Derivatives of Fluoran*, Phys. Rev. **8**, 674 (1916).

2. L. A. Jones and E. Huse, *On the Relation between Time and Intensity in Photographic Exposure*, J. Opt. Soc. Am. and Rev. Sci. Inst. **7**, 1079 (1923); **11**, 319 (1925).

L. A. Jones, E. Huse and V. C. Hall, *On the Relation between Time and Intensity in Photographic Exposure*, J. Opt. Soc. Am. and Rev. Sci. Inst. **12**, 321 (1926).

L. A. Jones and V. C. Hall, *On the Relation between Time and Intensity in Photographic Exposure*, J. Opt. Soc. Am. and Rev. Sci. Inst. **13**, 443 (1926).

L. A. Jones, V. C. Hall and R. M. Briggs, *On the Relation between Time and Intensity in Photographic Exposure*, J. Opt. Soc. Am. and Rev. Sci. Inst. **14**, 223 (1927).

J. H. Webb, *The Relationship between Reciprocity Law Failure and the Intermittency Effect in Photographic Exposure*, J. Opt. Soc. Am. **23**, 157 (1933).

3. L. A. Jones, *A Special Sensitometer for the Study of the Photographic Reciprocity Law*, J. Opt. Soc. Am. and Rev. Sci. Inst. **7**, 305 (1923).

4. J. H. Webb, *The Relationship between Reciprocity Law Failure and the Intermittency Effect in Photographic Exposure*, J. Opt. Soc. Am. **23**, 157 (1933).

5. W. W. Coblentz, *Measurements on Standards of Radiation in Absolute Value*, Bur. Stand. Pap. **11**, 87 (1915).

The Response of a Photographic Emulsion to Alpha-Rays

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The equation $D=D_{max}(1-e^{-c_1N})$ developed by Kinoshita for single-layer emulsions has been shown to hold for commercial emulsions. A derivation of this formula is given which shows that the probability constant c_1 should be the same for thick as for thin emulsions. A useful relation $s_0=k/\pi\rho^2$ between s_0, the number of grains under a sq. cm of emulsion surface, k, the number of grains in the depth of the emulsion, and $\pi\rho^2$, the average grain size has been deduced and tested. To eliminate the density due to fluorescence, chromic acid desensitization has been used. Photographic effects due to mechanical pressure have on these desensitized plates, been found to be reversed by alpha-rays as well as by the other radiations previously reported.

Average grain-size measured microscopically	$=0.14\mu^2$
$\pi\rho^2$ from desensitized plate No. 93	$=0.08$
$\pi\rho^2$ from desensitized plate No. 100	$=0.12$
$\pi\rho^2$ from $s_0=k/\pi\rho^2$	$=0.12$

Chromic acid desensitization has been found to be effective only for a limited time.

INTRODUCTION

The equation for single-layer emulsions

The response of a photographic emulsion to alpha-rays was first extensively studied by Kinoshita in 1909,[1] who, working with Rutherford, found a relation between the number of alpha-rays (N) and the photographic density produced (D) of the form

$$D=D_{max}(1-e^{-c_1N}) \tag{1}$$

where $D_{max}=3.7$, $c_1=1.181\times10^{-8}$ for an "instantaneous" plate, and $D_{max}=1.94$, $c_1=0.924\times10^{-8}$ for an "ordinary" plate. His analysis was, however, limited to special, thin emulsions, as difficulties were encountered in obtaining consistent results with commercial emulsions. Kinoshita found, as he expected, that for thicker emulsions the photographic density depended on the residual range of the alpha-rays which struck the emulsion but he was unsuccessful in determining the exact nature of the variation and attributed this failure to "inability to develop completely to the bottom of a thick emulsion even after three hours." An interpretation of the constant c_1 was obtained by assuming proportionality between the mass of metallic silver and the photographic density. Making this assumption, Eq. (1) becomes

$$m_1=m_0(1-e^{-c_1N}) \tag{2}$$

where N is the number of alpha-rays falling on 1 sq. cm to affect m_1 grains of silver beneath this area. Writing $m=$mass of 1 grain (μ) $\times$ the number of grains (s)/sq. cm of surface and differentiating Eq. (2), Kinoshita obtained

$$\delta s=c_1(s_0-s_1)\delta N. \tag{3}$$

For very small densities s_1 is negligible compared with s_0 and hence, in this case

$$\delta s=c_1s_0\delta N. \tag{4}$$

Now since the product of c_1, determined from the experimental curve, and s_0 determined from a microscopic grain count, was found to be approximately unity, then from Eq. (4), it followed that for these thin emulsions, the number of grains affected is equal to the number of alpha-rays striking the emulsion, and further, that c_1 was the probability of one of the s_0 grains/sq. cm being struck by one of the N alpha-particles falling on this area.

Some doubt seemed to be thrown on these deductions by some work of Michl[2] in 1912 and of St. Meyer and von Schweidler.[3] Experiments were, therefore, undertaken by Svedberg and

[1] S. Kinoshita, Proc. Roy. Soc. **A83**, 432–453 (1909).

[2] Michl, Wiener Ber. **121**, 1431 (1912).

[3] St. Meyer and von Schweidler, *Radioaktivitat*, p. 184, Leipzig, 1916.

Andersson[4] in 1921 which confirmed Kinoshita. But here again only special, single-layer plates were used.

The equation for "commercial" emulsions

In the present work, a commercial plate (the Eastman Process Emulsion) has been used. Difficulties (to be referred to below) which were at first experienced in obtaining consistent results were soon overcome and it was found that an equation of the form given by Kinoshita holds for commercial plates as well as for the special single-layer emulsion previously used. Different interpretations must, however, be given to the constants c_1 and s_0 for in Eq. (4) δs can no longer be expected to equal δn since with thick emulsions there will be several grains in the track of each alpha-particle, and in the determination of s_0 only the grains within the range of the alpha-ray are to be counted. But the surprising conclusion can at once be reached from this Eq. (4) that c_1 should be the same for thin as for thick emulsions if, as turns out to be the case, both $\delta s/\delta n$ (the number of grains in a track) and s_0 (the maximum number of grains capable of being affected) are proportional to the range of the alpha-rays in the emulsion.

A direct derivation of Eq. (1) may be made as follows:

Let us assume that when an alpha-ray enters a photographic emulsion it makes every grain within a cylinder of radius ρ and depth δ developable, where δ is the residual range of the particle in the given emulsion. We will not at present assume that ρ is the actual radius of a grain.

The probability that a particular grain will be affected by an alpha-particle which penetrates to a depth δ is merely the probability that this grain lies within the cylinder of action of the particle. This probability P is equal to the ratio of the volume of the cylinder to the volume of emulsion under 1 sq. cm and within a depth δ.

$$P=\pi\rho^2\delta/\delta=\pi\rho^2. \tag{5}$$

The number of grains made developable per second will be the product of three factors: (a) the number of grains yet unaffected; (b) the probability that a single alpha-particle will hit a given grain; (c) the number of alpha-particles falling. Thus, if G = the number of grains affected

$$dG=\pi\rho^2 dN(G_{\max}-G), \tag{6}$$

which yields on integration, remembering that for the evaluation of the constant of integration we have $G=0$ when $N=0$

$$G=G_{\max}(1-e^{-\pi\rho^2 N}). \tag{7}$$

Since now the photographic density is very nearly proportional to the number of grains affected[5]

$$D=D_{\max}(1-e^{-\pi\rho^2 N}), \tag{8}$$

which is identical with Kinoshita's original equation in that the constant is the probability that a given grain will be hit by a definite alpha-particle. Attention has already been called to the prediction that the probability constants in the two equations should be identical, i.e., $\pi\rho^2=c_1$. It is interesting to note that Eq. (4) shows $c_1=k/s_0$ where the emulsion is k grains in depth and s_0 is the number of grains below 1 sq. cm. We can therefore deduce a relation

$$\pi\rho^2=k/s_0, \tag{9}$$

which can be used to determine $\pi\rho^2$, the projective area of a single grain, if s_0 and k are known for a given emulsion.

This prediction can be tested with the following data for an Eastman Process Emulsion No. M-350 on which counts were made. $s_0=8.40\times10^9$; $k=10\pm1$; whence $\pi\rho^2=0.12\mu^2$; average cross-sectional area of grains measured microscopically $=0.14\mu^2$. This indicates that $\pi\rho^2$ is approximately equal to the average cross-sectional area of the grains and that therefore an alpha-particle must hit a grain to affect it. This agreement is highly satisfactory when the great difficulties in measuring the individual areas of the irregular grains and in determining their number are considered. The value of k was determined from the measured thickness of the emulsion, the range of polonium alpha-particle in the emulsion and the number of grains in a track.

[4] Svedberg and Andersson, *Relation Between Sensitiveness and Size of Grain in Photographic Emulsions: Effect of α and β rays*, Phot. J. **61**, 325–332 (1921).

[5] See L. A. Jones, *Photographic Sensitometry*, p. 54.

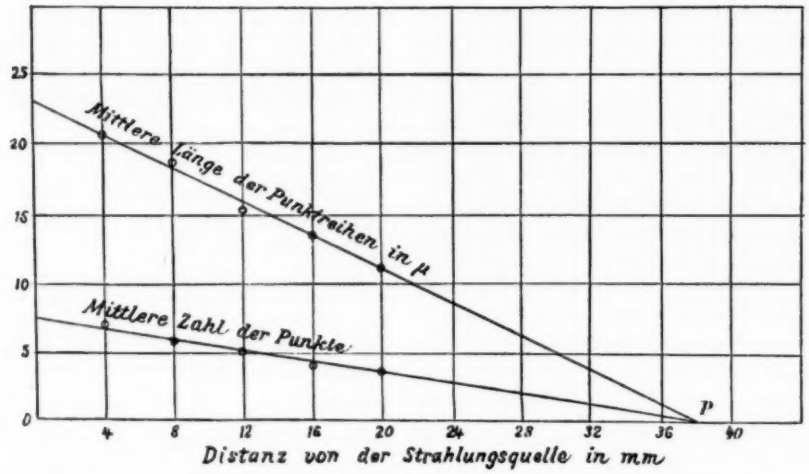

FIG. 1. Graph given by Michl which shows that both numbers of grains in an alpha-ray track and the length of the track are directly proportional to the range of the alpha-ray in the emulsion. (Reproduced from Akad. Wiss. Wien, Ber. **121**, 2a, 1431 (1912).)

The thickness of Emulsion No. M-350 was approximately 20μ.

The number of grains in the track of an alpha-particle

O. Mugge in 1909[6] was probably the first to notice that the track of an alpha-particle in a photographic emulsion consisted of a row of individual grains. Reinganum, in 1911,[7] again mentions this but a careful study of the relation between the range of the alpha-particles and the number of grains in a track came in 1912 with the work of W. Michl.[8] Two of his conclusions are of interest to us. (1) The number of silver grains in a track was directly proportional to the length of the track. (2) Both the number of silver grains in the tracks and the lengths of the tracks were directly proportional to the residual range which the alpha-particles have when they reach the emulsion. Michl's results are shown in Fig. 1. From the intersection of these curves on the distance axis, the range of the polonium alpha-rays which he used could be read and from the intercepts on the other axis, the number of grains in a track or the total length of a track in the emulsion which he used could be read directly.[9]

A simple and rapid method of obtaining data on the number of grains in a track is given by an examination of the halos produced in photographic plates which have been infected with a radioactive substance. If, for example, a metal disk on which polonium has been deposited is held above a plate and scraped with a needle, the polonium dust falling on the plate disintegrates and on development each dust particle is seen to be the center of a halo of the radial tracks first noticed by Mugge which are shown in Fig. 2. E. Mühlestein[10] pointed out that halos of more definite radius would be secured if the plate was covered by mercury immediately after it was infected so that all the alpha-ray tracks would have to be entirely in the emulsion instead of partly in air and partly in the emulsion as would be the case if the radioactive kernel projected slightly above the emulsion. Such a halo is shown in Fig. 3. It is, of course, smaller in diameter and emphasizes the necessity of using the mercury

[6] O. Mugge, Zentralbl. f. Mineralogie **71**, 144 (1909).

[7] M. Reinganum, Phys. Zeits. **12**, 1076 (1911).

[8] W. Michl, Akad. Wiss. Wien, Ber. **121**, 2a, 1431 (1912).

[9] The power of the tool furnished by these observations of Michl does not seem to have been fully appreciated. It is capable of being applied to a number of problems—see, for example, its application to the detection of isotopes. T. R. Wilkins and W. M. Rayton, Nature **130**, 475 (1932).

[10] E. Mühlestein, Arch. d. Sc. Phys. et Nat. Genev **44**, 63 (1917).

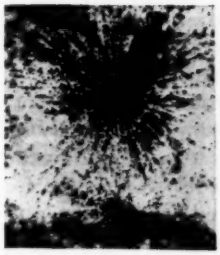

FIG. 2.

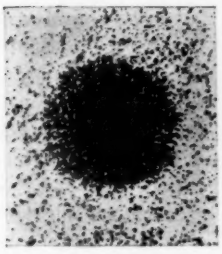

FIG. 3.

FIG. 2. Ordinary radioactive halo in a photographic emulsion.

FIG. 3. Radioactive halo produced by covering infected photographic plate with mercury.

Figs. 2 and 3 are reproduced from Rutherford, Chadwick and Ellis, *Radiations from Radioactive Substances*, p. 56.

covering in obtaining data on lengths of tracks. A halo as dense as Fig. 3 gives the range satisfactorily but is too dense for a grain count. Fig. 4 shows a mercury-covered halo for Eastman Process Emulsion. From a study of such halos the range of polonium alpha-rays in Emulsion No. M-350 was found to be 29μ and the number of grains in a track of this range to be 15. The stopping power of this emulsion is, therefore, 1380 times the stopping power of air.

With this information, we are now able to decide just how far the alpha-rays used will penetrate the emulsion. The photographic density produced will depend on this penetration.

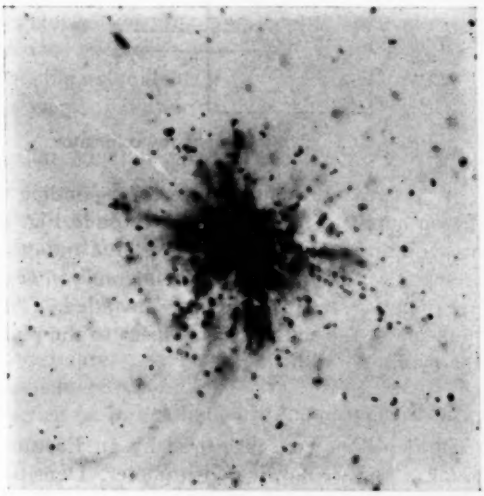

FIG. 4. Polonium halo in Eastman Process Emulsion.

DESCRIPTION OF APPARATUS

To secure data on the relation between the photographic density and the number of alpha-particles striking an emulsion, means must be provided for: (a) counting the number of alpha-particles; (b) varying the residual range of the particles; (c) measuring the density produced. Attention must be given, moreover, to the choice of a suitable emulsion and a study made of a development technique suited to this emulsion.

a. The counting of the alpha-particles

The use of a grid-glow tube, first suggested by Wilkins and Friend[11] affords the most convenient method of counting. The output of the Geiger chamber can be amplified and an automatic telephone counter operated. A run with the source screened gives the correction for "strays." The polonium source used in the part of our studies here reported gave on January 5, 1933, 80 particles/min. through an aperture of 3.64×10^{-5} sq. cm—the aperture being 6.93 cm from the source. The number of particles at later dates was calculated by taking account of the decay constant of polonium. The count was made with the source 6.93 cm from the opening in the Geiger chamber which was the exact position at which the photographic plate was later placed.

b. Method of varying the residual range

Kinoshita varied the range of the alpha-rays by interposing aluminum foils. It is easier, however, to secure this variation by putting the source and plate in a vacuum chamber and holding the pressure at a predetermined value. The use of foils and a high vacuum would have prevented the errors which we later found were being introduced by the fluorescence of the air through which the alpha-particles passed but the scattering produced by the foils and the complication due to secondary electron emission led us to feel that it was desirable to avoid these uncertainties, especially when we found it possible to desensitize the plate to the luminescence. Fig. 5

[11] T. R. Wilkins and F. B. Friend, J.O.S.A. **16**, 370 (1928).

FIG. 5. Experimental set-up for studying the response of a photographic emulsion to alpha-rays.

shows a mercury manometer and the auxiliary photoelectric cell equipment which was used. If the pressure rose, a small beam of light was no longer cut off by the mercury column and the photo-cell on which the light then fell operated a relay system which started the vacuum pump. The pressure was thus held within a millimeter of mercury for the week or more during which a run lasted. The residual air range with which the particles hit the emulsion was

$$[4-(p/76)6.93]\ \text{cm},$$

where 4 cm = range of polonium alpha-rays at 23°C, p = pressure in the vacuum chamber, 6.93 cm = distance from the source to the emulsion. The penetration of these rays into the emulsion is found by dividing this result by 1380, the value of the stopping power of this emulsion.

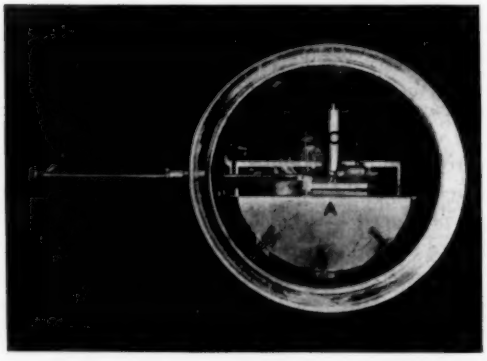

FIG. 6. Vacuum chamber in which polonium source and photographic plate were placed.

The polonium source and the photographic plate were mounted in a bell-jar located in the adjacent dark room shown at the right of Fig. 5. The general arrangement inside the bell-jar are shown in Fig. 6. The plate lay horizontally on the platform A. The source was mounted in the cylinder C. M is a small electromagnet for operating a slide which could prevent the rays from reaching the plate. For a new exposure the source could be moved to any position on the plate by means of two vacuum-tight screws, s_1 in the side and s_2 in the end of the bell-jar.

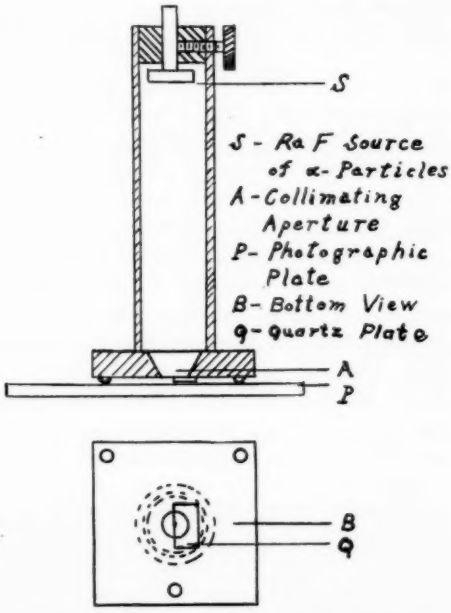

FIG. 7. Diagram of the alpha-ray collimator.

In this way all the exposures corresponding to a given family of curves such as those in Fig. 12 were obtained on the same plate and any discrepancies due to a variation in emulsion or of development technique were avoided. The mounting of the source with respect to the plate is shown in detail in Fig. 7.

c. The measurement of densities

The densities were measured by an Eastman Kodak Capstaff-Purdy densitometer. Densities could be read to ±0.02 but since such a densitometer must be calibrated in terms of a standard

strip which itself is only accurate to the same figure, accuracy of not more than ± 0.04 can be claimed for individual readings. The curve fitted to the group of individual readings probably approaches the true values more closely than this. The density due to fog, was less than 0.11 on plates No. 92 and No. 100 which are reproduced below.

d. Emulsion and development technique

The ideal emulsion for such studies would consist of one with as large a number as possible of spherical grains of uniform size. Obviously such an emulsion is impossible to obtain but a Process Emulsion is a fairly satisfactory approach to the ideal as can be seen from some typical size-frequency distribution curves published by Wightman, Trivelli and Sheppard.[12] Grain counts and a size-frequency curve were obtained for the particular batch of emulsion which we used.

Fig. 8 gives the results of a study which was made to determine the proper development-time to use on a fine-grained emulsion. The Hurter-Driffield curves for various development-times ranging from 2 to 10 minutes are there given. From these curves, various values of gamma are obtained which are shown in the time-gamma curve. The time-fog curve is also shown. On the basis of these curves it will be apparent that with a slow lantern plate, developed in "x-ray developer" for four minutes at 70°F, the results of the exposure will be utilized as fully as possible without the introduction of errors due to fogging.

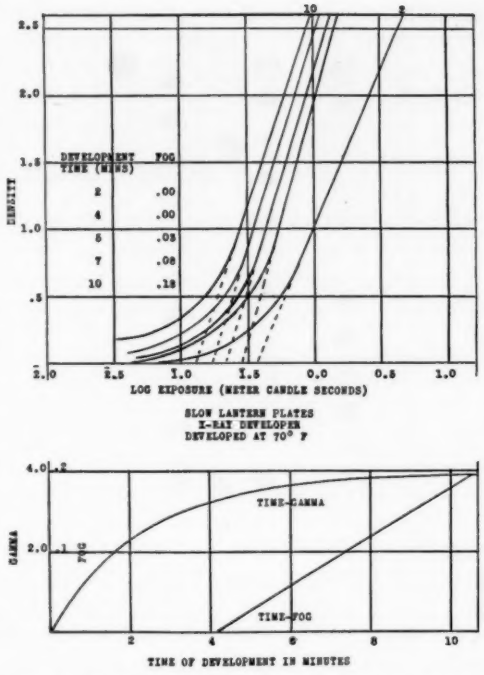

FIG. 8. *D*-log *E*, time-gamma and time-fog curves for determining proper development time.

e. The effect of luminescence

That alpha-rays produce luminescence in the air through which they pass has long been known. It was first studied by Sir William and Lady Huggins[13] who found the luminescence to coincide with the band spectrum of nitrogen, a result which has been confirmed by many later investigators. If we hope to get a pure alpha-particle effect either the experiment must be carried on in a vacuum or else the plate must be desensitized to this luminescence. Fig. 9 shows how large the density due to luminescence may be. In obtaining these exposures half the opening in the alpha-ray collimator (Fig. 7) was covered by a quartz plate. Thus both alpha-rays and light due to luminescence passed through one side of the opening but only light passed through the other. It can be seen that for long exposures and small penetrations the density due to luminescence is comparable to that due to the combined alpha-rays and luminescence.

The series of exposures shown in Fig. 10 were obtained in just the same way as those in Fig. 9 except that the plate was desensitized by bathing for one hour in a solution whose composition was 10 g $K_2Cr_2O_7$, 4 cc H_2SO_4 (conc.), water to 1 liter. The plate was then washed in tap water for 2½ hours to remove the desensitizing solution.

There are two added points of interest on these plates. In Fig. 9 a scratch can be seen which was made as one foot of the collimator dragged across the plate. The pressure of this foot

[12] E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard, J. Phys. Chem. **27**, 1–51 (1923).

[13] Proc. Roy. Soc. **A72**, 409 (1903); **A76**, 488 (1905); **A77**, 130 (1905).

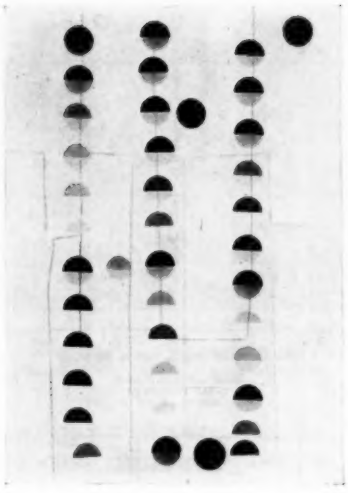

FIG. 9.

FIG. 10.

FIG. 9. Emulsion not desensitized. (Notice luminescence effect.)

FIG. 10. Emulsion desensitized. (Notice lack of luminescence effect except on right-hand column of exposures. These exposures, taken approximately two weeks after desensitization, show a partial recovery of sensitivity.)

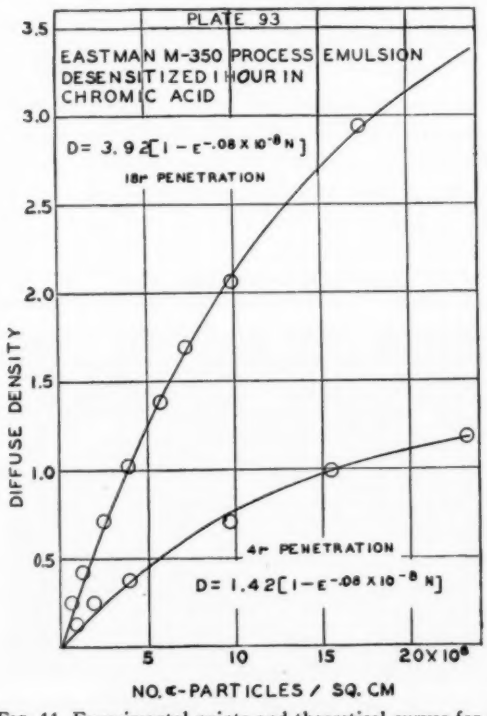

FIG. 11. Experimental points and theoretical curves for a desensitized Process Emulsion.

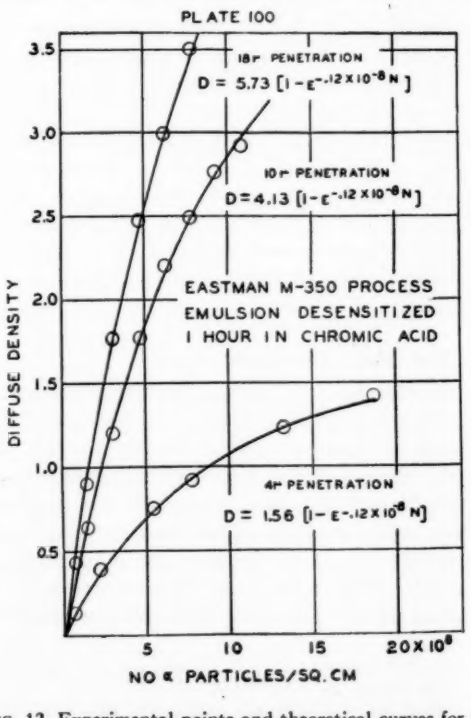

FIG. 12. Experimental points and theoretical curves for a desensitized Process Emulsion.

rendered the plate developable. In some desensitized plates this track instead of being dark against a light background is reversed. Such reversal has been reported[14] in many cases but as far as is known has not heretofore been observed for alpha-rays.

The second added point of interest concerns the recovery of sensitivity as can be seen in Fig. 10. In the right-hand column distinct evidence can be seen that the luminescence is once more affecting the plate. These last exposures were made approximately two weeks after the plate had been desensitized. If such a desensitizer is used it is suggested that it is an important part of the technique to use this scheme of covering half the field to make sure that the emulsion is retaining its insensitivity.

Results

Figs. 11 and 12 give the results of two experiments carried out on plates desensitized at different times. The equations fitting the results are shown. If it is recalled that the constant of the exponential term was indicated to be approximately equal to the average cross section of the grains, it seems that one result of desensitization is in effect to reduce the size of the grains, or at least to reduce the "receptor area" to alpha-particles.

Comparison of $\pi\rho^2$ and grain-size

grain-size (measured microscopically) $= 0.14\mu^2$
$\pi\rho^2$ from plate No. 93 (desensitized) $= 0.08$
$\pi\rho^2$ from plate No. 100 (desensitized) $= 0.12$
$\pi\rho^2$ from Eq. (9) $= 0.12$

The value of the exponential constant for each individual plate seems to be independent of the penetration as was predicted by the discussion incident to the deduction of Eq. (8). The variation of the numerical value of the constant between plates 93 and 100 is no more than might be expected when differences in desensitization, development and fixation are taken into account. The value of c_1 for this thick emulsion is surprisingly similar to that obtained by Kinoshita in 1909 for single-layer emulsions.

Fig. 13 shows data for a plate which was not desensitized. These curves where the densities

[14] R. W. Wood, Phil. Mag. 6, 577–587 (1903).

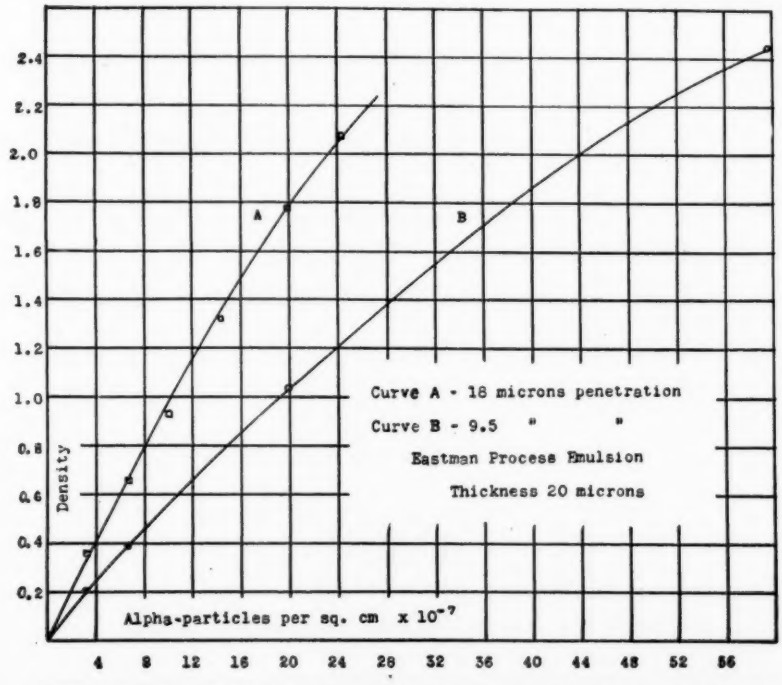

FIG. 13. Density—number of alpha-particles for a Process Emulsion not densitized.

are due to alpha-particles plus luminescence satisfy the equations

$$\therefore \qquad D=4.8(1-e^{-0.23\times10^{-6}N})$$

and

$$D=4.37(1-e^{-0.14\times10^{-6}N})$$

for the 18μ and the 9.5μ penetrations respectively. The value of the exponential constant is larger than it would be for a pure alpha-ray effect. It seems impossible at present to separate the two effects. It is even more complicated than an ordinary fog correction[15] since we have a combination of light passing through the emulsion with alpha-rays of limited penetration.

For pure alpha-ray effects, Eqs. (8) and (9) represent the experimental results with such precision that the response of a photographic emulsion to alpha-rays may well furnish a tool for investigations into various problems of photographic interest such as the rapid determination of the average grain size of an emulsion by Eq. (9), the variation of receptor area with desensitization, and real, or apparent, variations of the photometric constant due to a limited penetration of the radiation into the emulsion. The existence of some such anomaly as this last is indicated by the lack of proportionality between $D_{max.}$ and penetration.

The assistance of various members of the Eastman Kodak Research Laboratory in furnishing the size-frequency distribution data and in various helpful suggestions related to the photometric and desensitization problems involved is gratefully acknowledged.

[15] R. B. Wilsey, *Fog Corrections in Photographic Densities*, Phot. J. **65**, 454–458 (1925).